

THE
QUANTITATIVE SEPARATION
AND
DETERMINATION OF URANIUM

By
EDWARD FRANK KERN, B.S.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE OF
COLUMBIA UNIVERSITY

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INTRODUCTION.

The work described in this thesis was undertaken with the object of finding out the most accurate and satisfactory method for the technical estimation of uranium.

The great amount of work already done on uranium, during the past hundred and twenty years, has given rise to much material on the analytical behavior of uranium, which is scattered through the chemical literature. This has been classified under separations and determinations, and the essential features of the methods given as briefly as possible. Following the historical review, in each case, is a description of the experimental work, which relates to that particular separation or determination.

The research was drawn to a close by making a number of assays of uraninite, in which the different separations and estimations, worked out on pure solutions, were applied. These assays tested the methods on the most important ore of uranium, and thus collected the data in the form of analytical methods.

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May 1, 1901.

ACKNOWLEDGMENT.

This work was undertaken at the suggestion of Professor Edmund H. Miller, and carried out under his direction.

I take this opportunity to gratefully acknowledge my indebtedness to him for his valuable assistance and advice throughout the work, and to express my obligations for his encouragement given to the research, his interest in its progress, and for other valuable assistance rendered.

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THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.

URANIUM.

Uranium was discovered by M. H. Klaproth, who separated what he thought to be a new element from pitchblende—also known as uraninite—the principal ore of uranium. This was in 1789, and what he obtained was not the element, but its lower oxide— UO_2 . He named the element uranium in remembrance of the planet Uranus, which Herschel discovered in 1781.

From 1789 to 1795 much work was done on the investigation of uranium, but nothing new was discovered till 1840, when E. Péligot succeeded in isolating metallic uranium in powder form by heating uranous chloride (UCl_4) with metallic sodium.* He made a great number of experiments, the results of which proved that what was previously thought to be the element uranium was its lower oxide (UO_2), which plays the part of a base, a true inorganic radical. This discovery seems to have been an impetus to the further study of this element, as we find records in the different journals, of the years that follow, of several of the eminent chemists of the day investigating uranium and trying to find new methods for its estimation. The precipitant then used was ammonia, the principal reagent used at the present time for its determination.

Clemens Zimmerman was the next chemist of note to investigate uranium. He studied methods for isolating the metal, and methods for its estimation and separation from other elements, as well as prepared many of its salts, studying their chemical and physical properties.† This work covered a number of years, from 1877 to 1884. So 1877 marks the second revival of interest in the element uranium. The first revival was in 1789, when Péligot discovered it in uraninite or pitchblende. The third revival is the present time, brought on by the great industrial demand for uranium ores.

* *Leibig's Annalen der Chemie*, 41, 141. 1842.

† *Ibidem*, Vols. 119, 204, 213 and 214.

In 1854 the only use to which uranium was put was for making a very fine black for porcelain painting,* and from 1850 to 1866 it was much used in photography. At present its uses are for the preparation of acetate and nitrate salts which are used as chemical reagents, for the manufacture of a certain highly-prized canary-yellow colored glass, for the preparation of a pigment used for porcelain painting, and lastly for making a steel which has properties superior to nickel-steel. Metallic uranium is worth about \$90 a pound.† “Very recently it has been found that uranium carbide is superior to nickel and tungsten in the manufacture of high grade steels. The high price of metallic uranium, as is also the case with other of the rare metals, is due not so much to its rarity as to the fact that the process of isolating it and obtaining it in a pure state is costly. In most cases the high price of the rare metals is the cause of no serious effort having been made to utilize them industrially, therefore the process of extracting them has not been improved and cheapened. Witness aluminium and more recently thorium and cerium, the last two, which previous to their utilization in gas lighting by incandescence were worth about \$400 a pound.” Probably within the next few years the price of metallic uranium will be greatly lowered and its usefulness increased.

URANIUM MINERALS.

In the sixth edition of Dana's “Mineralogy” the following are given as the principal minerals of uranium:

1. URANINITE, also known as *pitchblende*, a mineral containing UO_3 , UO_2 , PbO , NiO , ThO_2 , Er_2O_3 , Y_2O_3 , Ce_2O_3 , Di_2O_3 , La_2O_3 , Fe_2O_3 , CaO , H_2O , and small amounts of the following: CeO , Bi_2O_3 , V_2O_5 , As_2O_5 , Sb_2O_5 , FeO , MnO , ZnO , P_2O_5 , MgO , and the gases *argon*, *helium* and *nitrogen*.

2. URANO-PHANE, a mineral of the following composition: SiO_2 , UO_3 , Al_2O_3 , Fe_2O_3 , PbO , BaO , CaO , SrO , MgO , K_2O , H_2O , and P_2O_5 .

3. URANO-TANTAL, a mineral containing: Ta_2O_5 , Nb_2O_5 , SnO_2 , WO_3 , UO_3 , Ce_2O_3 , Di_2O_3 , La_2O_3 , Y_2O_3 , Er_2O_3 , FeO , MnO , CaO , H_2O , TiO_2 , SiO_2 , ThO_2 , Fe_2O_3 and Al_2O_3 .

* Whitney's “Mineral Wealth of the United States.”

† Moniteur Industrial, 27, 44. 1900.

4. URANO-PILITE, a mineral containing: SiO_2 , SO_3 , UO_3 , CaO and H_2O .

5. TARBENITE, a mineral containing: P_2O_5 , As_2O_5 , UO_3 , CuO , CaO , H_2O and SiO_2 .

6. CARNOTITE, a vanadiferous uranium mineral containing: V_2O_5 , UO_3 , UO_2 , K_2O and H_2O , with small amounts of Fe_2O_3 , Al_2O_3 , CuO , PbO , CaO , BaO and P_2O_5 .

Until very recently the mineral which supplied the market with uranium was uraninite; but within the past two or three years carnotite, which occurs in great quantities in western Colorado, has been mined and shipped in large quantities to Germany and France. Its uses in the United States are at present very limited, the chief of which is in the preparation of uranium-steel on an experimental scale, the outcome of which is awaited with much interest.

SEPARATION OF URANIUM FROM MEMBERS OF THE FIFTH AND SIXTH GROUPS.

"To effect the separation of the oxides of the fifth group from those of the first three groups by means of hydrogen sulphide, it is only necessary that the reaction of the solution be acid, the nature of the acid to which the reaction is due being of no consequence. But to effect the separation of the oxides of the fifth group from those of the fourth group the presence of a free mineral acid is indispensable, otherwise zinc and, under certain circumstances, cobalt and nickel, may be coprecipitated."*

For the precipitation of cadmium by hydrogen sulphide, use a solution of 250 c.c. and add 10 c.c. of hydrochloric acid (sp. gr. 1.10). Ratio of free acid to total solution being 1 to 50. The other metals of the fifth group, except copper, comport themselves, in respect to being completely precipitated by hydrogen sulphide, similarly to cadmium, *i. e.*, they are not completely precipitated by hydrogen sulphide when much free acid is present. Lead requires the least amount of free acid to retain it in solution, then follow in order of succession cadmium, mercury, bismuth, copper and silver. When nitric acid is the acid used, the solution must be largely diluted. Warming of the solution during precipitation should not be done, especially if the solution is very acid.

* Fresenius' "Quantitative Chemical Analysis," p. 456. 1900.

In the precipitation of lead from a hydrochloric acid solution by hydrogen sulphide, it is necessary to dilute plentifully, otherwise the precipitation is incomplete. Even if the solution contains 2.5 per cent. of hydrochloric acid (sp. gr. 1.20), the whole of the lead is not precipitated.*

EXPERIMENTAL.

A solution of lead nitrate was made by dissolving 3 grams of the salt in distilled water and diluting to 500 c.c. Twenty-five cubic centimeters contained .09 gram of lead.

A solution of cupric chloride was made by dissolving 7 grams of the salt in distilled water and diluting to 500 c.c. Twenty-five cubic centimeters contained .116 gram of copper.

1. Twenty-five cubic centimeters of the copper solution and twenty-five cubic centimeters of the lead solution were measured into a beaker. Diluted to 250 c.c., 5 c.c. nitric acid (sp. gr. 1.42) added and hydrogen sulphide gas passed through the solution for forty-five minutes. The precipitate of sulphides of lead and copper were filtered off and thoroughly washed with hydrogen sulphide water. The filtrates from the two separate precipitations were tested for the presence of lead and copper. They were found to be free from these metals.

2. Two portions—each containing 25 c.c. of copper solution, 25 c.c. of lead solution, and 50 c.c. of standard uranium nitrate solution—were measured into beakers, and 5 c.c. nitric acid (sp. gr. 1.42) added. The solutions were diluted to 250 c.c., and hydrogen sulphide gas was passed through the cold solutions for one hour. The precipitates filtered off and thoroughly washed with hydrogen sulphide water. The precipitates were dissolved in hot hydrochloric acid and the presence of uranium tested by Sergius Kern's method † by means of potassium ferrocyanide. The precipitates were found to contain no uranium (uranium ferrocyanide dissolves readily in dilute hydrochloric acid, whereas the copper ferrocyanide is insoluble). The filtrates from the sulphides were slowly boiled till all H_2S was expelled, then 5 c.c. nitric acid (sp. gr. 1.42) was added and the boiling continued for a few minutes longer. Ammonia was added in slight excess to the hot solutions.

* *Journal für prakt. Chemie*, 67, 374.

† *Chemical News*, 33, 5. 1876.

The precipitates of ammonium uranate were filtered off, washed with hot dilute ammonium chloride solution (about 2 grams salt to 100 c.c. water), dried, ignited and weighed as U_3O_8 . The theoretical amount of uranium taken was .1925 gram, and the amounts determined in the filtrates were .1923 gram and .1928 gram.

3. Two more solutions were made up, each containing 25 c.c. copper solution, 25 c.c. lead solution and 30 c.c. standard uranium nitrate solution. To each solution was added 5 c.c. nitric acid (sp. gr. 1.42) and sufficient water to make 250 c.c. volume. Hydrogen sulphide gas was passed through the cold solutions for one hour, and the mixed sulphides filtered off and washed with hydrogen sulphide water. The precipitates were dissolved in hot dilute hydrochloric acid, the solution diluted to about 100 c.c. and potassium ferrocyanide added. No uranium was found to have been precipitated with the lead and copper. The uranium in the filtrates from the lead and copper sulphides was determined as in experiment No. 2, and weighed as U_3O_8 . The theoretical amount of uranium taken was .1155 gram; the amounts determined in the filtrates were .1157 gram and .1158 gram.

The above six experiments show that for the separation of lead and copper from uranium by means of hydrogen sulphide, the amount of concentrated nitric acid present should be 1 part in 50 parts of the solution.

SEPARATION OF VANADIUM FROM URANIUM.

Vanadium is one of the common associates of uranium, and especially so in the minerals which occur in Colorado. Carnotite, the most common of these minerals, has of late reached commercial importance.

The separation of vanadium from uranium presents very little difficulty unless phosphoric acid is present, in which case the separation is troublesome. Friedel and Cumenge* separated vanadium from uranium by evaporating the solution to dryness with nitric acid. The uranium was then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation, no phosphoric acid should be present as it renders the uranium oxide—which is in combination with it—insoluble in the dilute ammonium nitrate solution.

**American Journal of Science*, 10, 135. 1900.

The method for the separation of vanadium from iron by means of mercuric oxide and mercurous nitrate * has been used with success by A. C. Langmuir,† for the separation of vanadium from uranium in the analysis of carnotite. The finely divided mineral was dissolved in the smallest possible amount of nitric acid, and the silica filtered off. The solution was diluted to about 500 c.c. and the vanadium precipitated by means of mercurous nitrate as follows: The nitric acid solution was nearly neutralized with pure yellow mercuric oxide, and the vanadium then precipitated by the addition of a strong solution of mercurous nitrate. The solution was brought to boiling, after which it was filtered. (If chromium, tungsten or molybdenum are present they go down as mercurous salts with the mercurous vanadate.) The precipitate was washed with a warm dilute solution of mercurous nitrate, after which it was dried, ignited and weighed as V_2O_5 . The excess of mercury in the filtrate was removed by means of hydrogen sulphide gas. After expelling the hydrogen sulphide from the filtrate by slow boiling, the uranium was determined by the ordinary method.

SEPARATION OF URANIUM FROM MEMBERS OF THE THIRD AND FOURTH GROUPS, PARTICULARLY IRON.

Review of Methods.

The separation of uranium from the other members of the fourth group and those of the third group depends on the solubility of uranium hydroxide and sulphide in an excess of a strong solution of an alkali carbonate. The hydroxides and sulphides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in strong alkali carbonate solutions; in cold dilute solutions they are almost insoluble.

PISANI'S METHOD.‡—Ferric iron, aluminium, and chromium may be separated from uranium by means of an excess of ammonium carbonate. The uranium remains in solution while the iron, aluminium and chromium are precipitated as hydroxides. A small amount of iron, which passes into solution with the uranium, will

* Blair's "Chemical Analysis of Iron," 3d Ed., p. 200.

† Paper read before N. Y. Section of American Chemical Society, at March meeting.

‡ *Comptes Rendus*, 52, 106.

precipitate on allowing the solution to stand exposed to the air for several hours; or it may be directly precipitated by adding a few drops of ammonium sulphide to the filtrate.

M. Péligot says that in order to separate uranium from iron by means of ammonium carbonate you must operate with dilute solutions, for—according to Wöhler—the ferric hydrate is soluble in strong ammonium carbonate solution. Berzelius also stated that whatever may be the excess of ammonium carbonate employed, ferric hydroxide is completely precipitated by sufficiently diluting the solution.*

When iron alone was separated from uranium, Pisani precipitated both together with ammonia then treated the precipitate with a strong solution of ammonia carbonate. The ferric hydroxide was filtered off and a few drops of ammonium sulphide added to the filtrate in order to precipitate any iron which might have gone into solution with the uranium.†

ROSE'S METHOD.‡—This method is for the separation of uranium from iron, manganese, zinc, chromium, aluminium, copper and lead; but it is not suitable when nickel is present, as a small amount of this metal is apt to pass into solution with the uranium. The method is as follows: Add an excess of ammonium carbonate, to the solution containing the metals, then sufficient ammonium sulphide to wholly precipitate the iron. If the iron is in the ferrous state, it must previously be oxidized to the ferric state by means of hydrogen peroxide and boiling, or else by boiling with a few c.c. of nitric acid. All the metals, with the exception of uranium, are precipitated. Allow the precipitate to settle in a corked flask, and wash by decantation with water which contains a small amount of the precipitants.

The filtrate, which contains the uranium, is slowly heated to expel most of the carbon dioxide; then it is acidified by hydrochloric acid, and brought to boiling. The separated sulphur is filtered off, and the uranium oxidized by means of a few drops of nitric acid and again boiling. The uranium is precipitated with a slight excess of ammonia. Wash, dry, and ignite the precipitate, and weigh as oxide.

* Rose's "Practical Treatise of Chemical Analysis," 176. 1849.

† *Compte Rendus*, 52, 106.

‡ *Zeit. für Anal. Chemie*, 1, 410. 1862.

The above method was first used by Wöhler in 1852,* for separating uranium from zinc, nickel and cobalt.

Jannasch's Modification † of Rose's Method.—The uranium and iron are precipitated together with ammonia, and filtered off. The mixed precipitate is then digested in the warm for several hours with a mixture of ammonium carbonate and ammonium sulphide. Iron sulphide and uranium oxy-sulphide result, the latter being dissolved by the excess of ammonium carbonate to form uranyl ammonium carbonate $[UO_2CO_3 \cdot 2(NH_4)_2CO_3]$, which is very soluble. The iron sulphide is filtered off, washed with a dilute solution of ammonium sulphide, dried, ignited and weighed as Fe_2O_3 . To quickly drive off the sulphur from the iron, the ignited precipitate is mixed with dry ammonium carbonate and reignited. The filtrate, containing the uranium is evaporated to dryness in a porcelain dish, then digested with hydrochloric acid in order to dehydrate silica, which is apt to be present. The silica is filtered off, and the uranium is precipitated with ammonia, dried, ignited and weighed as oxide.

PATERA'S METHOD,‡ for separating uranium from iron, aluminium, manganese, zinc, calcium, etc. A rather dilute solution, containing the metals in the form of nitrates, is treated with a moderately large excess of sodium carbonate, and the solution brought to boiling so as to bring the double carbonate of uranium and sodium into solution. The mixed precipitate, containing the hydroxides of iron, aluminium, etc., is filtered off and washed with hot water. The filtrate, containing the uranium—after the expulsion of carbon dioxide—is precipitated with caustic soda, and the orange-colored precipitate of acid uranate of soda is washed with hot water and dried. The precipitate and the filter are separately ignited at redness in a platinum crucible, and after cooling, the contents of the crucible are transferred to a small filter and washed with hot water. It is then dried and reignited at redness. The weight of the $NaO \cdot 2U_2O_3$ multiplied by .883 gives the amount of U_3O_8 present.

Hugo Bornträger§ states that the precipitate of $NaO \cdot 2U_2O_3$, ob-

* *Leibig's Annalen der Chemie*, 56, 368.

† Jannasch's "Praktischer Leitfaden der Gewichts Analyse," Leipsic, p. 307. 1897.

‡ *Zeit. für Analyt. Chemie*, 5, 228. 1866.

§ *Zeitschrift für Analyt. Chemie*, 37, 436. 1898.

tinued by Patera's method, is liable to be seriously contaminated with silica. It is, therefore, advisable to dissolve the ignited precipitate in hydrochloric acid, filter off the silica, and reprecipitate the uranium with ammonia. After ignition it is weighed as U_3O_8 .

Potassium carbonate and potassium hydrate may be used in place of carbonate and hydrate of sodium in Patera's method.*

ZIMMERMAN-BRÜGELMAN METHOD † for the separation of uranium from iron. This separation depends on the fact that iron is completely precipitated by an excess of ammonium thiocyanate containing sodium bicarbonate, and the solubility of hydrated uranium dioxide in such a solution. The precipitation is made by first adding an excess of ammonium thiocyanate, then a saturated solution of sodium bicarbonate till the red color of the solution disappears. The metals should be in solution in the oxidized state. Bring the solution to boiling, filter off the ferric hydroxide and wash it with hot water till no reaction of sulphocyanide occurs on testing the washings. The precipitate is then dried, ignited and weighed as Fe_2O_3 . The excess of ammonium cyanide in the filtrate is destroyed by boiling and by adding nitric acid to acid reaction. Boiling is continued till all cyanogen and carbon dioxide is driven off. Neutralize the solution with ammonia and precipitate the uranium with freshly prepared ammonium sulphide. Weigh the uranium as oxide.

Wm. Crookes ‡ used sodium carbonate instead of sodium bicarbonate in the above method. The method otherwise is the same as outlined.

RHEINECK'S BASIC ACETATE METHOD § for separating uranium from iron. To a nitric acid solution of uranium and iron, add sodium carbonate till almost neutral reaction, then add an excess of sodium acetate. The solution is diluted to 50 times the weight of the oxides, and heated near boiling on a water-bath till all the iron is precipitated and the supernatant solution is clear. The acetate of uranium remains unaltered while the acetate of iron is decomposed and precipitates in the form of hydrated sesqui-oxide.

* Fremy's "Encyclopedic Chimique," p. 87. 1884.

† *Zeit. für Analyt. Chemie*, 20, 414, and *Leibig's Annalen der Chemie*, 199, 1-16. 1879.

‡ "Select Methods," p. 234.

§ *Chemical News*, 24, 233. 1871.

which carries along with it some uranium acetate in crystalline form. The uranium acetate is, however, readily soluble in boiling water, so it suffices that the precipitate be thoroughly washed with boiling water until no precipitate forms on adding ammonia to the washings. The filtrate and wash-water are united and the uranium precipitated with ammonia and weighed either as UO_2 or U_3O_8 .

Sodium hydrate may be used instead of sodium carbonate for nearly neutralizing the nitric acid solution previous to the addition of sodium acetate.*

PERCY H. WALKER METHOD,†—A large excess of hydrogen peroxide prevents the precipitation of uranium by sodium hydrate, but it does not affect the precipitation of iron as ferric hydroxide. This fact was applied to the separation of uranium from iron in the following manner: To the slightly acid solution, containing about 0.2 gram of uranium and iron, add 50 c.c. hydrogen peroxide, then slowly run this solution with constant stirring into a large casserole which contains a solution of 5 grams sodium hydrate in 50 c.c. water mixed with 50 c.c. hydrogen peroxide. The solution is diluted to about 400 c.c. with hot water and the precipitate of ferric hydrate is filtered off and washed with hot water. The filtrate, which contains all the uranium, is acidified with hydrochloric acid, evaporated to dryness on a water-bath and heated at 110° C. for one hour in order to dehydrate any silica which may be present. After the removal of the silica, the uranium is precipitated with ammonia and weighed as oxide.

ROSE'S METHOD‡ for separating uranium from iron by igniting the mixed oxides in a current of hydrogen. The uranium and iron in solution are oxidized by the addition of a small amount of nitric acid and boiling. Both metals are precipitated together with ammonia in excess. The precipitate is filtered, washed, dried, ignited and weighed. It consists of a mixture of Fe_2O_3 and U_3O_8 . The mixed oxides, after weighing, are placed in a boat and ignited in a current of dry hydrogen till the mass ceases to lose in weight, all the Fe_2O_3 having been reduced to metal and the U_3O_8 to UO_2 . The ignited mass is allowed to cool in a current of hydrogen and

* Dingler's "Polytechnisches Journal," S. C., 5. 1872.

† *Journal of the American Chemical Society*, 20, 514. 1898.

‡ *Annalen der Physik und Chemie*, 116, 252.

is then treated with dilute hydrochloric acid which dissolves the iron, leaving the UO_2 unacted upon. The residue of UO_2 is washed free of acid by hot water, dried, ignited and weighed. The iron in the filtrate is precipitated with ammonia and weighed as Fe_2O_3 .

L. Bercker² compared this method with that of Pisani and showed that the separation of uranium from iron by means of ammonium carbonate gave inaccurate results, as a double carbonate of uranium and ammonium is apt to contaminate the iron hydroxide. He stated that accurate results were obtained by the method outlined above.

M. A. Dute³ separated uranium from both iron and chromium by a modification of Rose's method. He stated that the separation of these three metals presented difficulty by the ordinary gravimetric method, but that very accurate results were obtained by a slight modification of the method which H. Saint-Claire Deville used for separating iron from aluminum. The solution, containing the uranium, iron and chromium, was precipitated with an excess of ammonia and heated till the excess was expelled. The mixed precipitate was washed, dried, and ignited in a porcelain boat. The ignited mass, consisting of U_3O_8 , Fe_2O_3 and Cr_2O_3 was allowed to cool, then weighed. After weighing, the boat was placed in a combustion tube and heated at redness in a current of dry hydrogen till all the Fe_2O_3 was reduced to metal, the U_3O_8 to UO_2 , while the Cr_2O_3 remained unchanged. The iron was removed from the mass by passing a current of hydrochloric acid gas in place of the hydrogen through the tube and heating at redness for about two hours. The UO_2 and Cr_2O_3 remain unaltered; the iron is changed to Fe_2Cl_6 and volatilized, depositing as white crystals in the colder part of the tube. After about two hours hydrogen was again run through the tube and the residue allowed to cool in the same. The mixture of UO_2 and Cr_2O_3 was weighed, then treated with warm dilute nitric acid which dissolved the brown UO_2 leaving the Cr_2O_3 which was washed, dried, ignited and weighed. The uranium may be directly estimated by precipitating it with ammonia and weighing as oxide. The iron may also be directly estimated by passing a mixture of steam and hydrochloric acid gas

² *Zeit. für Analyt. Chemie*, 19, 350.

³ *Compte Rendus*, 85, 281.

through the tube after the removal of the boat. The ferric chloride is carried along by the water as it condenses and is caught in a vessel. It is then precipitated and weighed in the ordinary way.

For this separation alkalis and alkali-earths should be absent.

"Uranous chloride [UCl_4] as obtained by heating metallic uranium in a stream of chlorine, or uranous oxide in hydrochloric acid, consists of dark green octahedra with metallic luster. It volatilizes at red heat forming a red vapor. It deliquesces in the air, and dissolves with hissing. On evaporating the solution, uranous hydroxide remains." * This statement seems to place a doubt on the separation of iron from uranium by Ditte's modification, or else it shows that the temperature at which the mixture is ignited in hydrochloric acid gas should be less than redness.

GIBB'S METHOD † for separating uranium from cobalt, nickel and zinc. To the neutral or nearly neutral solution of the chlorides of uranium, cobalt, nickel and zinc, add sodium acetate in excess and a few drops of acetic acid. The solution is boiled, and a rapid current of hydrogen sulphide is passed through the boiling solution for half an hour. Every trace of the cobalt, nickel and zinc is precipitated as sulphides while the whole of the uranium—and any manganese, if present—remains in the boiling solution. The precipitate is thrown on a ribbed filter and quickly washed with cold hydrogen sulphide water. The precipitate is easily washed, and though the sulphides of cobalt and nickel formed in this manner are more easily oxidized than when precipitated by sodium sulphide from a boiling solution, they will be found to present no difficulty as regards oxidation upon the filter. If manganese is in the filtrate it may be determined by boiling with hydrochloric acid and precipitating it in the usual manner with sodium carbonate. The uranium in the filtrate is determined by the ordinary method.

Gibbs stated that the separation of uranium from cobalt, nickel and zinc, as outlined above, gave excellent results, and that the method is much simpler than Rose's "Barium Carbonate Separation."

ROSE'S BARIUM CARBONATE METHOD ‡ for the separation of ura-

* Richter's "Inorganic Chemistry," p. 387. 1896.

† Silliman's *American Journal of Science and Art* [2]; 39, 62. 1865.

‡ "Chimie Analytique—Analyse Quantitative," H. Rose, p. 248. 1862.

nium from manganese, cobalt, nickel and zinc. Barium carbonate completely precipitates uranium from uranic solutions, even in the cold. The reaction is essentially different from that of manganese, cobalt, nickel and zinc, and is a means of effecting a separation of uranium from these metals. For this separation the uranium is oxidized to the uranic state by means of a few drops of nitric acid and boiling. The solution should contain some free acid—either nitric or hydrochloric acid—and barium carbonate, which is diffused in water, is added in excess. Use a corked flask and allow the solution to stand in the cold for twenty-four hours. At first the flask is vigorously shaken for a few minutes, after which it is frequently shaken. In order to prevent any cobalt or nickel from being carried down by the uranium, some ammonium chloride is added. The precipitate is washed well with water. It is then dissolved in hydrochloric acid, the solution diluted and the excess of barium precipitated with dilute sulphuric acid. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide.

C. Rammelsberg* stated that barium carbonate cannot be advantageously used for the precipitation of uranium when manganese and zinc are present; but it may be employed for the separation of uranium from cobalt and nickel.

EXPERIMENTAL.

Zimmerman's "Ammonium Thiocyanate Method" for the separation of uranium from iron was devised with the view of overcoming the objection which is raised against Pisani's "Ammonium Carbonate Method," that is, the solubility of the ferric hydrate when an excess of ammonium carbonate is used. The method which Zimmerman proposed was by the use of ammonium thiocyanate and sodium bicarbonate.†

For the purpose of comparing this method with the methods ordinarily used for separating uranium from iron, six solutions were made up, each containing .1540 gram uranium and .0901 gram iron. The solutions were diluted to 150 c.c. and oxidized by boiling with 1 c.c. nitric acid (sp. gr. 1.42). An excess of a freshly

* *Chemical Central Blatt*, p. 806. 1884.

† *Leibig's Annalen der Chemie*, 199, 10-16. 1879.

prepared solution of ammonium thiocyanate was added, thus giving the solution a dark red color. A saturated solution of an alkali carbonate was then added until the dark red color of the solution changed to brown, due to the color of precipitated ferric hydrate. After the addition of the carbonate, the solutions were boiled for about five minutes, then filtered.

To the first three solutions was added more sodium bicarbonate than was necessary to destroy the dark red color. The ferric hydrate, which at first was reddish brown and voluminous, changed to greenish ferrous hydrate, which on standing turned black, and a scum of red basic ferric hydrate floated on the surface of the solution. The solution had an odor of hydrocyanic acid. The precipitates were filtered and washed with warm water. The filtrates after standing exposed for about two hours were coated with a scum of basic ferric hydrate which was filtered off. The filtrates from the second filtrations on standing exposed over night were again coated with basic ferric hydrate. This showed that the amount of iron, dissolved by the excess of sodium bicarbonate, was in large quantities, so the solutions were emptied and the metals not determined.

Solution No. 4 was treated according to the method as outlined in the *Zeitschrift für Analytische Chemie*, Vol. 20, page 414. Sodium bicarbonate and ammonium thiocyanate were used as the precipitants, the sodium bicarbonate being added till the dark red color of the hot solution changed to reddish brown. The precipitate of ferric hydrate was filtered off and washed with hot water. The filtrate from the iron was yellow in color, due to uranium.

The precipitate was dissolved from the filter with warm dilute hydrochloric acid (sp. gr. 1.066) and the solution evaporated to fumes with 20 c.c. sulphuric acid (sp. gr. 1.84). The iron was reduced at boiling temperature with metallic zinc, then titrated with a standard solution of potassium permanganate. The amount of iron determined was .0231 gram, which is .0770 gram less than was taken. The filtrate containing the uranium (and also iron) was evaporated to 100 c.c., and the sodium bicarbonate and ammonium thiocyanate destroyed by slowly adding nitric acid to acid reaction. The solution was evaporated to dense white fumes with 20 c.c. sulphuric acid (sp. gr. 1.84), diluted to about

100 c.c. and reduced at boiling temperature by metallic zinc. It was diluted to 500 c.c., and titrated with a 1% potassium permanganate solution. The amount of permanganate used was 25.4 c.c. which corresponds to .0787 gram of uranium or .1447 gram in excess of the amount taken. This excess was not uranium, but iron which went into solution with uranium. No uranium was found with the ferric hydrate precipitate.

Solution No. 5 was precipitated by Crooke's modification of Zimmerman's method,* using normal sodium carbonate instead of sodium bicarbonate. The precipitate of ferric hydroxide which formed was very voluminous and had a slight red color, due to some thiocyanate which was carried down. It was filtered and thoroughly washed with boiling water. The filtrate was almost colorless. The precipitate was dissolved from the filter with dilute acid, and the solution titrated by standard permanganate solution as in the above determination. 20.6 c.c. of permanganate solution was required, which corresponds to .1133 gram of iron, or .0232 gram too much. The reduced solution was green in color, due to uranium which was carried down by the iron. The amount of uranium in the filtrate was determined as outlined under solution No. 4. The amount determined was .1082 gram, or .0458 gram less than was taken. No iron was found in the filtrate with the

Solution No. 6 was precipitated by ammonium thiocyanate and ammonium acid carbonate $[(NH_4)_2CO_3 \cdot 2NH_4HCO_3]$, instead of ammonium thiocyanate and sodium bicarbonate which was used by Zimmerman. The precipitate of iron was thoroughly washed with hot water, and dissolved in hot dilute hydrochloric acid. The solution was evaporated to fumes with 20 c.c. sulphuric acid (sp. gr. 1.84) diluted to about 100 c.c., and reduced by metallic zinc. 4.6 c.c. of a 1% permanganate solution was used, which corresponds to .0253 gram iron, or .0648 gram less than was taken for the experiment. The filtrate from the ferric hydrate, containing the uranium (and the iron which went into solution) was evaporated to 100 c.c., acidified with nitric acid, and evaporated to dense white fumes with 20 c.c. sulphuric acid (sp. gr. 1.84). The solution was diluted to 100 c.c. reduced by metallic zinc, and titrated with

$n/100$ permanganate solution. The amount of permanganate used (25.1 c.c.) corresponds to .2952 gram uranium, .1412 gram more than was taken. The excess of permanganate went to oxidize the iron which was not precipitated by the thiocyanate and ammonium carbonate.

The method of Zimmerman for the separation of uranium from iron, as shown by the above experiments is far from satisfactory and very unreliable. As it gave no promise of a complete separation of uranium from iron, the investigation was stopped.

SEPARATION OF URANIUM FROM IRON BY MEANS OF ETHER.

In 1892 J. W. Rothe* used ether for separating iron from aluminium, manganese, cobalt, nickel and copper. This separation depends on the solubility of ferric chloride in aqueous solution with hydrochloric acid, when it is shaken up with ether, and then allowing the two solutions to separate. The ferric chloride is taken into solution by the ether, whereas the chlorides of the other metals remain in the lower aqueous hydrochloric acid layer. When iron is in the ferrous condition, Rothe found that it was not taken into solution by the ether, but remained with the other metals in the aqueous solution.

Since 1892 the "ether separation" of iron has been applied to analyses other than those of iron and steel. Sargent† used ether for separating iron from nickel in the analysis of nickel-steel, thereby obtaining most satisfactory results. Langmuir‡ later applied the "ether separation" of iron from nickel to the analysis of nickel ores. He found that it was a means of separating iron from copper, manganese, aluminium, cobalt, nickel and zinc. At the close of his article, Dr. Langmuir made the statement that "the separation of iron from uranium by ammonium carbonate and ammonium sulphide is far from satisfactory, especially so if the uranium be small in amount. Possibly, in this case as well, the ether extraction of iron may result in a decided improvement." And so it has.

The separation of iron from uranium by means of ether was

* *Chemical News*, 66, 182.

† *Journal of American Chemical Society*, 854. 1899.

‡ *Ibidem*, p. 102. 1900.

tried, and, as the result, a clean and rather rapid separation has been worked out. This separation depends on the complete extraction of ferric chloride (in an aqueous hydrochloric acid solution) by ether which is free from alcohol, and the retention of uranyl chloride in the aqueous hydrochloric acid solution.

Before undertaking the separation of iron from uranium by means of ether, two solutions containing uranium alone were three times treated with ether, in order to demonstrate the solubility of uranyl chloride in ether. The method of treatment was as follows: 25 c.c. of standard uranium nitrate solution (.09625 gram U) was twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with dilute hydrochloric acid, and the solution heated till everything had gone into solution. After allowing to cool, the solution was poured into a 250 c.c. separatory funnel and shaken with ether. The hydrochloric acid used for solution No. 1 was of specific gravity 1.10 (one part acid sp. gr. 1.20 and one part distilled water). The hydrochloric acid used for solution No. 2 was of specific gravity 1.133 (two parts acid sp. gr. 1.20 and one part water). In each case three extractions with ether were made. The volume of the solutions at first was about 40 c.c. To each was added 50 c.c. of pure ethyl ether, which had previously been shaken up with hydrochloric acid of the same strength as that used in the solution. The ether and the aqueous hydrochloric acid solution were shaken together for about seven minutes, occasionally releasing the pressure which was due to evaporation of ether. The two layers were then allowed to separate, and the lower aqueous hydrochloric acid solution was drawn off into a lower 250 c.c. separatory funnel. The ether layer remaining in the upper funnel was twice shaken up with 10 c.c. of hydrochloric acid of same specific gravity as that used for the solution. The washings were allowed to separate, after which they were run into the lower funnel containing the aqueous hydrochloric acid solution of uranium. The "ether treatment" of the uranium solution was twice repeated, making three treatments in all. The first treatment was with 50 c.c. ether, the second with 40 c.c. and the third with 40 c.c. The ether in each case (after separating from the lower aqueous hydrochloric acid solution of uranium) was twice washed with 10 c.c. of hydrochlo-

ric acid of same specific gravity as that used for the solution. The washings were added to the main solution.

The uranium in the aqueous hydrochloric acid solution was determined by allowing the ether, which it contained, to evaporate spontaneously by leaving it stand exposed for several hours, after which it was twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry residue was taken up with a small amount of dilute hydrochloric acid (sp. gr. 1.10) and evaporated to dense white fumes with 20 c.c. sulphuric acid (sp. gr. 1.84). The solution was then washed into a small Erlenmeyer flask, diluted to about 125 c.c. and reduced at boiling temperature with about 50 grams of pure metallic zinc. The reduction being continued for about one and a half hours until the solution was a clear green color, resembling the color of a dilute solution of nickel chloride. The reduced solutions, after diluting to about 500 c.c., were titrated with $n/100$ potassium permanganate. Solution No. 1 contained .09588 gram uranium and solution No. 2 contained .09643 gram, the theoretical amount of uranium taken being .09625 gram. These experiments showed uranyl chloride to be entirely insoluble in ethyl ether which is free from alcohol.

The experiments which follow were made with solutions containing both uranium and iron. The procedure was as follows: A measured amount of a standard uranium nitrate solution and of a standard ferric chloride solution was placed in a small beaker and the solution twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with about 10 c.c. dilute hydrochloric acid (sp. gr. 1.10) and heated till all salts were dissolved, but not long enough to lose any of the acid by volatilization. After the solution had cooled, it was poured into a 250 c.c. separatory funnel and the beaker rinsed out with dilute hydrochloric acid (sp. gr. 1.10). The rinsings were added to the separatory funnel till the volume of the solution had reached 50 c.c. Fifty c.c. of ether, free from alcohol and previously shaken up with hydrochloric acid (sp. gr. 1.10), were added and agitated for about ten minutes, occasionally relieving the pressure in the funnel. After thoroughly shaking together, the two solutions were allowed to separate and the lower aqueous hydrochloric acid solution of uranyl chloride, containing some iron, was drawn off catching it in another

separatory funnel. The ether solution of ferric chloride was washed twice with 10 c.c. dilute hydrochloric acid (sp. gr. 1.10) and the washings, after allowing to separate, were run into the funnel containing the uranium.

On determining the amount of iron extracted from the hydrochloric acid solution by the ether, it was found that by one extraction all the iron was not separated from the uranium; about 10.5 per cent. of the amount taken remaining in the aqueous solution with the uranium.

The amount of iron extracted was determined by allowing the ether to evaporate spontaneously, then twice evaporating almost to dryness with hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with 10 c.c. dilute hydrochloric acid (sp. gr. 1.10) and the solution evaporated to dense white fumes with 15 c.c. sulphuric acid (sp. gr. 1.84). The solution was washed into an Erlenmeyer flask, reduced at boiling temperature by metallic zinc, and titrated with $\frac{n}{100}$ potassium permanganate.

The aqueous hydrochloric acid solution containing the uranium—also some iron—was twice evaporated to dryness with hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with 10 c.c. dilute hydrochloric acid, evaporated to dense white fumes with 20 c.c. sulphuric acid (sp. gr. 1.84), and reduced and titrated in the same manner as solutions No. 1 and No. 2.

On finding that all of the iron was not separated from the uranium by one "ether extraction," two extractions were next made on a solution containing .1155 gram uranium and .0901 gram of iron. The first extraction was made in the same manner as outlined above, and the second as follows: The solution in the lower separatory funnel was again shaken for about seven minutes with 50 c.c. ether. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid layer run into a second funnel. The ether solution was twice washed with 10 c.c. hydrochloric acid (sp. gr. 1.10), and the washings caught in the second funnel. The ether solution was run into a beaker which contained the ether from the first extraction. After distilling off the ether the iron was determined by titration with $\frac{n}{100}$ potassium permanganate solution.

Not all the iron was separated from the uranium by two "ether

extractions," about 3.5 per cent. of the amount taken remained in the aqueous solution with the uranium.

The next five separations of iron from uranium were made by using hydrochloric acid of specific gravity about 1.10 (1 part acid, sp. gr. 1.20, and 1 part distilled water). In all cases three "ether extractions" were made whereby practically complete separations of iron from uranium were obtained. The solutions contained from .0901 to .1802 gram iron and from .0962 to .2310 gram uranium. The amount of metals in their respective solutions was determined volumetrically in the same manner as previously outlined. The amounts determined did not vary more than 0.3 per cent. of the theoretical amounts taken.

The next five experiments were made by varying the strength of the hydrochloric acid used. The procedure was the same as above, making three extractions with ether. The solutions contained both uranium and iron. For the first three solutions, hydrochloric acid of specific gravity about 1.133 (2 parts acid, sp. gr. 1.20, and 1 part distilled water) was used. For the last two solutions hydrochloric acid of specific gravity about 1.066 (1 part acid, sp. gr. 1.20, and 2 parts distilled water). The separation in both cases, of iron from uranium, was incomplete. When hydrochloric acid of specific gravity 1.133 was used, the amount of iron remaining with the uranium, after three "ether extractions," was about 6.0 per cent. of the amount taken. When hydrochloric acid of specific gravity 1.066 was used, the amount of iron which remained with the uranium after three "ether extractions," was about 25.0 per cent. of the amount taken.

The most complete separations of iron from uranium by means of ether are evidently obtained by using hydrochloric acid of specific gravity 1.10. This is the same strength as was found by Speller* to be the best for the separation of iron from copper, manganese, aluminium, chromium, cobalt and nickel by means of ether.

When rather concentrated hydrochloric acid (sp. gr. 1.133) was used for the solution of the chlorides of iron and uranium, it was noticed that on diluting the aqueous solution—after agitating with ether—quite an amount of ether separated. This shows

* *Chemical News*, 83, 124. 1901.

that the more concentrated the hydrochloric acid, the greater is its affinity for ether. This, also seems to explain the reason why iron is not readily separated from uranium by means of ether when strong hydrochloric acid is used to bring their chlorides into solution; the iron being retained by the large quantity of ether which remains with the acid solution.

The results obtained are shown in the following table.

SEPARATION OF IRON FROM URANIUM BY EXTRACTION WITH ETHER.

Experiment No.	Specific gravity of HCl used.	Volume of solution at 1st extraction.	Number of ether extractions made.	Ether used for			Theoretical amount of uranium taken.	Amount of uranium determined in aqueous H ⁺ solution.	Theoretical amount of iron taken.	Amount of iron determined in ethereal extract.
				1st extraction.	2d extraction.	3d extraction.				
1	1.10	40 cc.	3	50 cc.	40 cc.	40 cc.	.09625	.09588		
2	1.133	40 "	3	50 "	40 "	40 "	.09625	.09643		
3	1.10	50 "	1	50 "			.11550	.13171	.09010	.08415
4	1.10	50 "	1	50 "			.11550	.14700	.09010	.07700
5	1.10	50 "	2	50 "	50 "		.11550	.12466	.09010	.08690
6	1.10	40 "	3	50 "	50 "	50 "	.09625	.09643	.09010	.08993
7	1.10	25 "	3	75 "	50 "	35 "	.11550	.11525	.09010	.09020
8	1.10	25 "	3	75 "	50 "	35 "	.09625	.09643	.18021	.18029
9	1.10	25 "	3	75 "	50 "	35 "	.19250	.19228	.09010	.08993
10	1.10	25 "	3	75 "	50 "	35 "	.23099	.23069	.09010	.09037
11	1.133	40 "	3	50 "	50 "	50 "	.09625	.10584	.09010	.08663
12	1.133	25 "	3	75 "	50 "	35 "	.11550	.12068	.09010	.08580
13	1.133	25 "	3	75 "	50 "	35 "	.19250	.20815	.09010	.08250
14	1.066	25 "	3	75 "	50 "	35 "	.09625	.20933	.18022	.12705
15	1.066	25 "	3	75 "	50 "	35 "	.23099	.27224	.09010	.07150

SEPARATION OF URANIUM FROM THE ALKALI AND THE ALKALINE EARTH METALS.

Review of Methods.

If* a solution containing uranium, alkalies and alkaline earths be precipitated with ammonia a portion of the alkalies and alkaline earths is carried down by the ammonium uranate. In this case, in order to separate the alkalies and the alkaline earths from uranium, it is necessary that the precipitate be dissolved in hydrochloric acid and the solution evaporated to dryness in a platinum crucible. The mass is then gently ignited in a current of hydrogen, after which the chlorides of the alkalies and alkaline earths are extracted with warm water. The residue is dried, reignited and the uranium weighed as oxide.

* Fresenius' "Quantitative Chemical Analysis," 6th edition, p. 533.

Instead of treating the precipitate with hydrochloric acid, it may be cautiously heated with ammonium chloride, and the chlorides of the alkali and alkaline earths then extracted with warm water.

The * mixed chlorides should not be heated above low redness, as uranyl chloride is volatile at a red heat.

Hillebrand† found that it is possible to completely separate uranium from the alkalis and alkaline earths by several precipitations with ammonia.

G. ALIBIGOFF'S METHOD for separating uranium from calcium, strontium, magnesium and the alkalis.‡ The use of mercuric oxide for quantitative analytical purposes was first suggested by Volhard. In 1885, Alibigoff studied the action of mercuric oxide on uranium solutions and found a means of separating uranium from the alkali and alkaline-earth metals. He showed that neither ammonium sulphide, nor ammonium carbonate when followed by an addition of ammonium oxalate—as proposed Foullon—can be successfully employed for the separation of uranium from calcium. When ammonium sulphide is the precipitant, some calcium always goes down with the uranium. When ammonium oxalate—in the presence of ammonium carbonate—is the precipitant, a small amount of uranium is carried down by the calcium oxalate. The latter method is, however, preferable to the first for the separation of uranium from calcium.

Alibigoff states that a complete separation of uranium from calcium, strontium, magnesium and the alkali metals can be effected by the use of mercuric oxide. It, however, does not afford a separation of uranium from barium. The method is as follows: To the boiling solution, which contains a small amount of ammonium chloride or ammonium nitrate add freshly prepared mercuric oxide (in the form of an emulsion) till all the uranium is precipitated as a mixture of uranium hydrate and basic mercuric uranate, which is insoluble in cold water. An excess of mercuric oxide should be avoided. After adding the precipitant, the solution is boiled for a few minutes and then rapidly cooled by placing the vessel in

*Fremy's "Encyclopédie Chimique," p. 86. Rose's "Quantitative Chimie Analytique," I, p. 246. 1859.

†*American Journal of Science*, 10, 136. 1900.

‡*Leibig's Annalen der Chemie*, 1886, 233, 147.

cold water. Care should be taken not to touch the side of the beaker with the stirring-rod, as then the precipitate attaches itself to the beaker and is very difficult to remove. Shake around in preference to stirring with a rod. After the solution is cooled it is allowed to stand till the supernatant liquid is colorless. Wash the precipitate by decantation with a cold dilute solution of ammonium chloride.

If the solution contains a relatively large quantity of calcium or strontium the precipitate should be boiled with water which contains some ammonium chloride. If magnesium is present the solution must be boiled with ammonium chloride before adding the mercuric oxide.

The precipitate of uranium hydrate and basic mercury uranate, after thorough washing, is placed along with the filter in a platinum crucible. It is first cautiously heated, after which the temperature is gradually raised and finally ignited over a "blast." The residue consists of pure U_3O_8 .

The separation of uranium from the alkali metals by this method does not give any undue trouble, but when calcium and strontium are present they are rather hard to rid from the uranium precipitate. This difficulty is overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium in the filtrate are determined by the ordinary methods after the removal of the mercury by hydrogen sulphide.

Magnesium may be separated from uranium by means of ammonium sulphide in the presence of ammonium chloride* and also by ammonia in the presence of an excess of ammonium chloride. The latter method is the one ordinarily used.† To the solution containing uranium and magnesium, add ammonium chloride and boil. When the solution becomes clear, add a slight excess of ammonia to the hot solution and continue boiling for a few minutes. Filter while hot and wash the precipitate with hot water containing ammonium chloride. Dry, ignite and weigh the uranium as oxide.

* *Zeitschrift für Analyt. Chemie*, 4, 384. 1865.

† Fremy's "Encyclopédie Chimique," p. 86. 1884.

SEPARATION OF URANIUM FROM BARIUM, STRONTIUM AND CALCIUM, BY MEANS OF SULPHURIC ACID.*

The metals should be in solution as chlorides, having present the smallest possible amount of free hydrochloric acid. To the moderately dilute solution, add sulphuric acid, then alcohol, which precipitates the barium, strontium and calcium, in the form of sulphates. The uranium in the filtrate is precipitated with ammonia and weighed as oxide.

The separation of uranium from barium, strontium and calcium, may be brought about by precipitating the uranium with freshly prepared ammonium sulphide (free from CO_2).†

SEPARATION OF URANIUM FROM THE ALKALI AND ALKALINE EARTH METALS BY ELECTROLYSIS OF ACETATE SOLUTION.

Uranium is a very difficult metal to separate from the alkalis and alkaline earths by gravimetric methods; but by electrolyzing an acetate solution of these elements a perfect separation can be effected.‡ It can be readily separated from sodium, potassium, rubidium, cerium, magnesium, calcium, strontium and barium. This method was used by E. F. Smith for separating uranium from the alkalis, the alkaline earths and the rare earths in the analysis of certain rare minerals.

The method is as follows:§ To the solution containing about 0.1 gram of uranium add 0.5 c.c. of glacial acetic acid, and dilute to 40 c.c. Electrolyze at a temperature of 70°C . with a current of $\text{N.D.}_{40} = 0.18$ ampère and 3 volts. The uranium is completely precipitated in 6 hours. The solution poured from the deposit showed no uranium when it was evaporated to dryness and the residue tested for that metal. The cathode was a 50 cc. platinum crucible, and the anode a long platinum wire spiral formed by wrapping the wire around a pencil. The deposit consisted of hydrated proto-sesquioxide of uranium ($\text{U}_3\text{O}_4 + \text{H}_2\text{O}$), which was ignited and weighed as U_3O_8 .

* Fremy's "Encyclopédie Chimique," p. 86. 1884.

† Fresenius' "Quantitative Chemical Analysis," p. 534.

‡ *American Chemical Journal*, 1, 329. 1879.

§ *Journal of American Chemical Society*, 279. 1898.

A very peculiar property of uranium is that it is not deposited as metal on the cathode, but as the hydrated proto-sesquioxide. Molybdenum is the only other metal known which, like uranium, is deposited as oxide on the cathode.

EXPERIMENTAL.

This research was made in order to fully confirm the reliability of the electrolytic method for the estimation of uranium and its separation from the alkalies, and also to find the conditions which are best suited for rather dilute solutions.

The cathodes, for the first six experiments, when a current of $N.D_{140} = .6 @ .7$ ampère was employed, were two platinum dishes of about 250 c.c. capacity. For experiments Nos. 7 to 10, the cathode was a platinum dish of about 150 c.c. capacity.

The anodes were made of heavy platinum wire. One was made of 30 cm. of No. 12 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The other anode was made of 37 cm. of No. 14 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The results obtained by the use of either anode were the same.

Storage cells were the source of current.

For the electrolysis, a measured amount of standard uranium nitrate solution was measured into a cleaned and weighed platinum dish. A known amount of sodium acetate and of acetic acid was added, and the solution diluted to a definite volume. After heating to about 60° C., the current was started and the electrolyzation continued till the solution was clear and colorless, and no uranium was indicated when about 2 c.c. of the electrolyte was removed and tested with potassium ferrocyanide in the presence of hydrochloric acid. As soon as all the uranium was precipitated, the current was interrupted and the electrolyte was emptied into a beaker. The black deposit was several times washed with warm distilled water. The electrolyte and washings were then poured through a fluted filter, so as to prevent the loss of any particles of the deposit which are apt to be removed during washing. The filter was washed with warm water, dried over a Bunsen flame, ignited, and added to the dish. The dish was ignited at "redness" for about fifteen minutes, after which it was allowed to cool in a desiccator. The dish was weighed and the final weight

taken when it had remained on the balance pan for about five minutes, thus allowing its weight to become constant.

The deposit consisted principally of black hydrated proto-sesquioxide of uranium [$U_3O_4 \cdot 3H_2O$], which on ignition changed to U_3O_8 .

At the beginning of the electrolysis, the deposit formed as yellow uranic hydroxide, but as the deposition continued it changed to the black hydrated proto-sesquioxide.

The results obtained* are :

Experiment No.	Grams of sodium acetate.	Amount of glacial acetic acid.	Dilution c.c.	Current.		Temperature °C.	Time in hours.	Theoretical amount of U_3O_8 taken.	Weight of deposited U_3O_8 .
				N. D. _{.140} = Ampère.	Volts.				
1	2	.7 c.c.	200	.55	5	68-70	8	.1098	.1095
2	2	12 drops	200	.60	5	70	7	.1098	.1097
3	2	.5 c.c.	200	.60-.65	8-6	68-75	5	.1098	.1100
4	2	.5 c.c.	200	.65	8-7.3	65-67	5½	.1318	.1319
5	2	.5 c.c.	200	.65	7.5-6	68-70	5	.1318	.1318
6	2	.5 c.c.	200	.60-.65	8-5.5	69-71	5½	.1318	.1320

These results were obtained by electrolyzing a solution of 200 c.c. volume with a current of N.D._{.140} = .55-.65 ampère.

The results obtained, when a solution of 125 c.c. was electrolyzed with a current of N.D._{.100} = .70-1.50 ampère, are as follows :

Experiment No.	Grams of sodium acetate.	Amount of 50 per cent. acetic acid.	Dilution C.C.S.	Current N. D. _{.100} = Amperes.	Temperature °C.	Time in hours.	Theoretical amount of U_3O_8 taken.	Weight of deposited U_3O_8 .
8	1.	2 c.c.	125	.70-.85	80-85	6	.1361	.1363
	2.	2 "	125	.70-.93	70-80	6½	.1814	.1816
9	2.	2 "	125	.95-1.50	70-75	7½	.2268	.2270
10	0.3	1 "	125	.90-1.30	73-80	8	.2268	.2260

According to the above results, the best conditions for the electrolytic precipitation of uranium from a rather dilute acetate solution are as follows : To the solution containing about .10 gram of

* This part of the work, including experiments 1-6, was done under the direction of Prof. E. F. Smith at the University of Pennsylvania, during April, 1900.

U_3O_8 add from 1 to 2 grams of sodium acetate (if alkalis are present, no sodium acetate is needed) and from 1 to 2 c.c. of 50 per cent. acetic acid, or if glacial acetic is used only half the quantity is needed. Dilute to from 125–200 c.c., heat to about $65^\circ C$. and electrolyze with a current of $N.D._{100} = .60-.70$ ampère and 6 to 8 volts. The uranium is completely precipitated in from 5 to 7 hours.

With solutions containing about .15 gram of U_3O_8 , more current is necessary and the best conditions are: Add from 1 to 2 grams of sodium acetate, and from 1 to 2 c.c. of 50 per cent. acetic acid, dilute the solution to 125 c.c. and electrolyze with a current of $N.D._{100} =$ from .70 to 1.0 ampère. The temperature of the solution should be about 65 to $70^\circ C$. After the current is started no heat need be outwardly applied as the current itself keeps the solution heated. The time required for the complete precipitation of about .15 gram of U_3O_8 is from $6\frac{1}{2}$ to $7\frac{1}{2}$ hours.

When solutions containing more than .15 gram of U_3O_8 were electrolyzed some difficulty was experienced in precipitating all within 8 hours by a current not exceeding $N.D._{100} = 1$ ampère. With a current greater than this the deposits were very spongy and peeled from the dish. So the amount of U_3O_8 in solution should not exceed .15 gram.

The electrolytic precipitation of uranium has been used a number of times for the estimation of uranium, and the results obtained were concordant with those obtained by precipitating it gravimetrically.

The simplicity of the electrolytic method for the determination of uranium, and the short time required for making the determination is in favor of this method.

SEPARATION OF URANIUM FROM PHOSPHORIC ACID.

Review of Methods.

REYNOSO'S METHOD.*—The uranium compound should be in solution as nitrate, having a small amount of free nitric acid present. Dilute to about 150 c.c., add a small strip of pure metallic tin, and boil. The phosphoric acid unites directly with the tin to form

* *Leibig's Annalen der Chemie*, 81, 368. 1852.

oxyphosphate of tin which is insoluble. The precipitate is filtered off and thoroughly washed. The filtrate is made alkaline with ammonia, and the precipitate which forms is treated with acetic acid. If it does not entirely dissolve, nitric acid is then added and a small strip of pure metallic tin.* Heat the solution to boiling and filter off the oxyphosphate of tin, and wash with warm water. The precipitate rarely contains any uranium. The tin in the filtrate is removed by means of hydrogen sulphide. The filtrate from the tin sulphide is boiled till all hydrogen sulphide is expelled, after which the uranium is determined by any of the ordinary methods.

W. Hintz† had occasion to investigate this method and stated that a complete separation of phosphoric acid from uranium is effected by means of metallic tin.

KNOPF AND ARENDT METHOD.‡—The separation of uranium from phosphoric acid may be effected by fusing the ignited mass of uranium and phosphoric acid with a mixture of potassium cyanide and potassium carbonate. Treat the fused mass with warm water, dissolving out the phosphoric acid as soluble alkaline phosphate. The uranium is left as protoxide, which is reignited and weighed, or else dissolve it in acid and precipitate by ammonia. The phosphoric acid is precipitated with magnesia mixture and weighed as magnesium pyro-phosphate.

Hintz§ used sodium carbonate in place of potassium carbonate, and obtained very satisfactory results.

E. REICHARDT'S METHOD.||—The substance containing uranium and phosphoric acid is dissolved in nitric acid, the solution diluted, and silica filtered off. The filtrate is made alkaline with ammonia, then acidified with acetic acid and heated to boiling, thereby precipitating all the phosphoric acid as uranyl-ammonium phosphate.¶ The precipitate is filtered off, washed, and dissolved in a solution of sodium carbonate. The solution is added to a

* Frey's "Encyclopédie Chimique," p. 86. 1884.

† *Leibig's Annalen der Chemie*, 151, 216. 1869.

‡ *Chemical Centralblatt*, 773. 1856.

§ *Leibig's Annalen der Chemie*, 151, 216. 1869.

|| *Zeitschrift für Analyt. Chemie*, 8, 116. 1869. *Bulletin de la Société Chimique*, 20, 347. 1873.

¶ Provided the uranium is in excess.

solution of magnesia mixture, which precipitates the phosphoric acid as magnesium-ammonium phosphate.

The filtrate is evaporated to dryness, the residue taken up with acid, and the solution boiled. Ammonia is added in slight excess, and the precipitate of ammonium uranate is filtered, washed, dried, ignited and weighed as oxide.

When iron is present* the substance is dissolved in hydrochloric acid, and a few drops of nitric acid added in order to completely oxidize the iron. Dilute the solution, bring to boiling and add an excess of sodium carbonate which precipitates the iron. The phosphoric acid in the filtrate is removed by adding magnesia mixture, and allowing the solution to stand in the cold for twenty-four hours. The solution is then filtered, and the phosphate ignited and weighed as magnesium pyro-phosphate. The filtrate from the phosphate is rendered acid with hydrochloric acid, and boiled till all carbon dioxide is expelled. The uranium is precipitated and weighed as usual.

FRESENIUS AND HINTZ METHOD.†—Various difficulties are experienced in separating uranium and iron from ores which contain phosphoric acid and arsenic acid, when the ordinary methods are followed. The use of potassium ferrocyanide is found to overcome these difficulties by the following procedure: After the removal of the silica, have the solution feebly acid with hydrochloric acid, add an excess of potassium ferrocyanide, then saturate with sodium chloride causing the precipitate to subside quickly. If copper is present it is precipitated along with the uranium and iron. The precipitate is first washed by decantation, then on the filter with a dilute solution of sodium chloride. After washing, it is treated with a solution of caustic potash which transforms the ferrocyanides into hydroxides. Filter, wash by decantation with warm water, and rinse on the filter with water which contains a small amount of ammonium chloride. The washing is continued till no potassium ferrocyanide is recognized in the washings (after acidifying with HCl). The mixed hydroxides are then treated with hydrochloric acid, and should completely dissolve. If any insoluble residue remains, treat it with a strong solution of caustic

* *Zeitschrift für Analyt. Chemie*, 8, 116. 1869.

† *Ibidem*, 34, 437. *Chemical News*, 72, 206. 1895.

potash, going through with the same treatment as before. The solution by hydrochloric acid is free from phosphoric and arsenic acids.

The uranium, copper and iron are separated as follows: The hydrochloric acid solution—which contains these three metals—is nearly neutralized with ammonia, and ammonium carbonate added in excess, which precipitates the iron as hydroxide. The precipitation should be made in the cold. The greater part of the carbon dioxide in the filtrate from the iron is removed by boiling, after which the copper is precipitated by means of hydrogen sulphide. The filtrate from the copper is slowly boiled till all the hydrogen sulphide is expelled. The uranium is precipitated by ammonia and weighed as oxide.

FREIDEL AND CUMENGE* separated phosphoric acid from uranium by dissolving the substance in nitric acid, and precipitating the phosphoric acid with ammonium molybdate. The uranium in the filtrate was determined by precipitating it three times with ammonia and weighing as oxide.

This method was used† for estimating the amount of phosphoric acid in precipitates of uranous phosphate, which were formed by electrolysis. The sample was dissolved in 30 c.c. nitric acid (sp. gr. 1.42) and 3 c.c. hydrochloric acid (sp. gr. 1.20). When iron was present, the sample was dissolved in a mixture of 20 c.c. hydrochloric acid (sp. gr. 1.20) and 10 c.c. nitric acid (sp. gr. 1.42). The solution was diluted to about 100 c.c., and nearly neutralized with ammonia. A few drops of nitric acid were added to clear the solution, making it slightly acid, then to the hot solution (not above 65° C.) 50 c.c. of molybdic solution‡ for every decigram of P_2O_5 present. Digested at 65° C. for an hour and a half, filtered, and washed the yellow precipitate with cold water. The filtrate was tested for phosphoric acid by adding more molybdic solution and reheating at 65° C. The yellow precipitate of ammonium phospho-molybdate was dissolved from the filter with ammonia and hot water, and washed into a beaker to a

* *American Journal of Science*, 10, 135. 1900.

† At the University of Pennsylvania in 1900.

‡ Prepared according to the formulas given in the "Official Methods of the U. S. Agricultural Chemists."

bulk not exceeding 100 c.c. Nearly neutralized with hydrochloric acid, cooled, and magnesia mixture added drop by drop from a burette, stirring all the while. After about twenty minutes 30 c.c. ammonia (sp. gr. 0.96) were added and the solution allowed to stand in the cold for three hours. The precipitate of magnesium ammonium phosphate was filtered and washed with dilute ammonia (2.5 c.c. ammonia and 100 c.c. water) till free from chlorides. The precipitate was dried, ignited and weighed as magnesium pyrophosphate.

The uranium in the filtrate, from the ammonium phosphomolybdate, was determined by three precipitations with ammonia, and weighing it as U_3O_8 .

THE DETERMINATION OF URANIUM.

DETERMINATION OF URANIUM AS OXIDE.

Review of Methods.

The precipitant which Pélégot used in 1840 for the estimation of uranium was ammonia, the principal reagent used for that purpose at the present time. The method which is ordinarily used is as follows: * The uranium must be in solution in the uranic state. If uranous salts are present, add a few drops of nitric acid, and nearly boil the solution in a platinum or porcelain dish and then precipitate it with a slight excess of ammonia. The yellow precipitate which forms is the hydrated ammonium uranate † $[(NH_4)_2U_2O_7 \cdot xH_2O]$, or $(NH_4)_2O \cdot 2UO_3 \cdot xH_2O$. It should be filtered hot and without interruption, and washed with a dilute solution of ammonium chloride which prevents the filtrate passing through turbid. The precipitate is dried and ignited separate from the paper, after which the paper is added and ignited. The crucible should be placed in a slanting position during ignition, so as to completely oxidize the precipitate to U_3O_8 . The lid is then placed on the crucible and the ignition continued a few minutes longer. The crucible is allowed to cool in a desiccator, and weighed.

Ammonium uranate is soluble in alkali carbonate solutions, and slightly soluble in pure water; but in water containing ammonia,

* Fresenius' "Quantitative Chemical Analysis," 6th ed., p. 281.

† *Chemiker Kalender*, p. 270. 1899.

ammonium nitrate or ammonium chloride it is insoluble.* The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents the precipitation of ammonium uranate. †

If the solution contains any alkalies or alkaline earths, a portion of these will be precipitated along with the uranium. ‡ In this case the precipitate should be dissolved in hydrochloric acid, the solution evaporated to dryness in a platinum crucible and the residue gently ignited in a current of hydrogen. The uranyl chloride is converted into uranous oxide (UO_2) and the alkali and alkaline earths remain as chlorides. The cold mass is treated with warm water, which dissolves all except the uranous oxide. The residue is thoroughly washed with warm water, after which it is ignited in hydrogen and finally weighed as UO_2 ; or it may be ignited in the air and weighed as U_3O_8 .

Rose § separated the alkalies and alkaline earths from the uranium precipitate by mixing the ignited precipitate with dry ammonium chloride and cautiously heating. The heating should not be carried above "redness," as above this temperature uranyl chloride (UO_2Cl_2) is volatile. The ignited mass is allowed to cool, extracted and washed with warm water, and the residue ignited and weighed as UO_2 or U_3O_8 as directed above.

If any sulphuric acid is present in the precipitate it may be removed by the addition of a small quantity of ammonium carbonate and the precipitate reignited. The ammonium carbonate prevents the loss of uranium by volatilization as uranium sulphate.

Rose || states that the reduction of U_3O_8 to UO_2 by ignition in an atmosphere of hydrogen is an excellent means of ascertaining its purity for the purpose of control. In case of a large quantity of U_3O_8 the ignition must be several times repeated and the residue occasionally stirred with a platinum wire, while cooling increases the current of hydrogen so as to prevent the absorption of oxygen by UO_2 . By intense heating the property of spontaneous oxidation in the air is destroyed.

* Comey's "Dictionary of Chemical Solubilities."

† Fresenius' "Qualitative Chemical Analysis," 219.

‡ *Ibidem*, 6th edition, p. 533.

§ Rose's "Quantitative Chimie Analytique," I, 246. 1859. Fremy's "Encyclopédie Chimique," 86. 1884.

|| Fresenius' "Quantitative Chemical Analysis," 6th edition, p. 282.

Zimmerman * states that after working with the oxides of uranium, he reached the following conclusions: The oxide U_3O_8 is permanent only when heated in a current of oxygen and allowed to cool in the same. If U_3O_8 is heated in air and quickly cooled it loses a small and variable quantity of oxygen, which is greatly increased if the oxide is allowed to cool in an indifferent gas. When this gas is nitrogen or carbon dioxide, the U_3O_8 is gradually decomposed and finally completely converted into UO_2 .

BERTHIER'S METHOD.†—The reagent next in importance to ammonia for the estimation of uranium is ammonium sulphide, which was first used (in 1840) by Berthier for this purpose. He also knew that the presence of carbonates prevented the precipitation of uranium by ammonium sulphide. Rose,‡ a few years later, states that he obtained complete precipitations of uranium by the use of ammonium sulphide, provided the solution was previously saturated with ammonia and no alkali carbonates were present. The precipitate which usually formed was black, but when a large excess of ammonium sulphide was used the precipitate changed to reddish brown color, due to a mixture of $(UO_2)S$ and UO_2 . He also found that a complete separation of uranium from the alkalies and alkaline earths was obtained by means of ammonium sulphide.§

In 1865, A. Remele studied the method for the estimation of uranium by the use of ammonium sulphide and found that the best results were obtained by the following procedure: || The ammonium sulphide should be fresh and kept well corked, as it absorbs carbon dioxide when exposed to the atmosphere. To the nearly neutral ammonical solution, add an excess of yellow ammonium sulphide and keep the solution near boiling for an hour, in order to convert the $(UO_2)S$, which is first formed, into a mixture of UO_2 and sulphur. This precipitate is rapidly dissolved by alkali carbonates and by tartaric acid. It is slightly soluble in pure water, is soluble in dilute, but insoluble in absolute, alcohol. It is readily soluble in acids, even acetic acid.¶ The presence of ammonium chloride or

* *Leibig's Annalen der Chemie*, 232, Pt. 3.

† *Ibidem*, 46, 184.

‡ Poggendorf's "Annalen," 116, 352.

§ *Zeitschrift für Analyt. Chemie*, 1, 411. 1862.

|| *Ibidem*, 4, 379.

¶ *Comey's "Dictionary of Chemical Solubilities."* 1896.

ammonium nitrate assists the precipitation of $(\text{UO}_2)_2\text{S}$, as it is less soluble in these solutions. The precipitate, containing all the uranium, is filtered off and washed with cold or hot water containing a small amount of ammonium sulphide and ammonium chloride or nitrate. Wash first by decantation and finally on the filter. The precipitate during washing passes to yellow uranic hydroxide. It is dried, then roasted to remove all the sulphur and finally converted into U_3O_8 , by ignition in the air, or into UO_2 , by ignition in a current of hydrogen and allowing to cool in same.

C. Winkler* made a comparison of this method with "Péligot's Ammonium Method" and states that the precipitation of uranium by pure ammonium sulphide is trustworthy.

Products of Decomposition of Uranyl Sulphide.

C. Zimmerman† studied the decomposition and transformation products of uranyl sulphide and stated that the metals of the so-called "ammonium sulphide group" display a varying permanence in their sulphur compounds, decreasing from zinc sulphide through cobaltous, nickelous, manganous, ferrous sulphides, and becoming slightest in the sulphur compound of uranium. He stated that the uranium may be regarded as a connecting link between those metals which are precipitated as sulphides by ammonium sulphide, and those which are precipitated as hydroxides by the same reagent, just as lithium is the transition between the alkalies and the alkaline earths.

Zinc, nickel and cobalt—whose oxides are less numerous—retain sulphur more firmly than does iron or manganese, while uranium—which forms no less than nine oxides—has the least affinity for sulphur.

Remele‡ stated that when uranyl sulphide was left in contact with ammonium sulphide the liquid assumed a dark brown color. This color, says Zimmerman,§ is due to the solubility of uranyl sulphide in ammonium carbonate contained in the ammonium sul-

* *Chemical News*, 43, 153. 1881.

† *Leibig's Annalen der Chemie*, 204, 204. 1880.

‡ Poggendorf's "Annalen," 124, 120.

§ *Leibig's Annalen der Chemie*, 204, 224. 1880.

phide. When the ammonium sulphide contains a considerable amount of thiosulphate the red sulphide described by Remele is formed; but when thiosulphate is absent only the dark precipitate results. The thiosulphate in the reagent is due to the oxidation of ammonium sulphide by atmospheric oxygen.

EXPERIMENTAL.

Precipitation of Uranium by Ammonia.—For each determination a measured amount of standard uranium nitrate solution was run into a beaker and enough distilled water added to bring the volume to from 150 to 200 c.c. The solutions were brought to boiling and a few drops of nitric acid added, and the uranium precipitated by adding an excess of ammonia to the hot solution. The precipitates which formed were a bright lemon-yellow color and settled rapidly. The precipitates were allowed to settle, and several times washed by decantation and twice on the filter with warm dilute ammonium chloride solution (2 grams salt to 100 c.c. water), after which they were dried in a hot oven, and ignited and weighed as oxides.

The following table gives the conditions observed:

THE THEORETICAL AMOUNT OF URANIUM TAKEN WAS 0.1925 GRAM.

Experiment No.	Approximate dilution.	Salts present.	Crucible in which ignited.	Weighted as:	Weight of U_3O_8 .	Uranium equivalent of U_3O_8 .	Ignited in hydrogen for:	Weight of UO_2 .	Uranium equivalent of UO_2 .
1	200 c.c.	NH_4Cl	Platinum.	U_3O_8	.2242	.19130			
2	200 "	"	"	"	.2268	.19252			
3	150 "	"	"	"	.2269	.19260			
4	150 "	"	"	"	.2266	.19235			
5	175 "	"	"	"	.2268	.19252	2 hours.	.2191	.19329
6	175 "	$\begin{cases} NH_4Cl \\ CHCl_3 \end{cases}$	"	$\begin{cases} U_3O_8 \\ UO_2 \end{cases}$	.2267	.19243	$\frac{3}{4}$ "	.2179	.19223
7	175 "	$\begin{cases} NH_4Cl \\ CHCl_3 \end{cases}$	Porcelain.	U_3O_8	.2269	.19260	$2\frac{1}{2}$ "	.2207	.19479
8	150 "	NH_4Cl	Platinum.	"	.2268	.19252	1 "	.2211	.19505
9	150 "	"	"	"	.2270	.19268	$\frac{3}{4}$ "	.2221	.19593
10	150 "	$\begin{cases} NH_4Cl \\ Alcohol \end{cases}$	Porcelain.	"	.2280	.19353			
11	175 "	$\begin{cases} NH_4Cl \\ Alcohol \end{cases}$	"	"	.2270	.19268			
12	175 "	NH_4Cl	Platinum.	UO_2			$\frac{1}{2}$ "	.2180	.19232
13	150 "	"	Porcelain.				1 "	.2240	.19761

U_3O_8 multiplied by .84884 gives the uranium equivalent; UO_2 multiplied by .88218 gives the same. These are the factors obtained by taking the atomic weight of uranium as 239.6 and that of oxygen as 16.0.

For all the above precipitations the solutions, of from 150 to 200 c.c. volume, were made decidedly acid with from .5 to 1 c.c. nitric acid (sp. gr. 1.42), brought to boiling and ammonia added in excess. Some of the solutions were boiled for about fifteen minutes after the precipitation by ammonia, while others were filtered directly without boiling. The boiling caused the lemon-yellow colored voluminous amorphous precipitate to change to a more crystalline form, less voluminous and of a slightly darker color. The precipitates which were boiled were much easier to filter and wash, and were less liable to pass through, which usually happened when boiling was not done.

The presence of chloroform or alcohol (as recommended by some chemists) did not assist the precipitation, but the presence of ammonium chloride or ammonium nitrate was essential. These latter two salts can be added either in the solid form, or else by adding an excess of acid and neutralizing. Five to ten grams were added previous to the addition of ammonia.

Some of the precipitates were ignited separate from the paper, and others were ignited without separating from the paper. The results obtained, whether the precipitates were ignited separate from the paper or not, were identical. This shows that it is unnecessary to ignite the precipitate and the filter paper separately, as is recommended by the German chemists.

When the uranium was weighed as U_3O_8 , the precipitates together with the filter paper were placed in a crucible and slowly ignited till the paper had completely burned; then the ignition was continued for about fifteen minutes in a "blast-flame," and allowed to slowly cool in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation. The results were the same whether porcelain or platinum crucibles were used.

In all directions given in text-books and journals for weighing uranium as oxide, it is recommended that the dry precipitate of

ammonium uranate be strongly ignited over a "blast" to U_3O_8 , and allowed to slowly cool in a gradually decreasing flame and finally in a desiccator. It is then weighed, and as a means of ascertaining its purity for the purpose of control, it is reignited in a current of pure hydrogen and reduced to its lower oxide, UO_2 . This was tried, but only in one case was it possible to completely reduce U_3O_8 to UO_2 , even when the ignition in hydrogen was continued for two hours. This time (experiment No. 6) the reduction was brought about by using a platinum crucible and igniting strongly in a current of pure hydrogen over the hottest "blast" that could be obtained. When a porcelain crucible was used in which the ignition was made, the reduction did not proceed so far as when a platinum crucible was used. The reason for this is explained by Roberts-Austen* as follows: "Saint Claire Deville and Troost discovered that hydrogen and hydrocarbons pass through platinum at a red heat." The further reduction of U_3O_8 , when a platinum crucible is used, would seem to indicate that the hydrocarbons of the flame play as important a part in the reduction as the hydrogen itself. It was impossible to obtain a single complete reduction of the precipitate to UO_2 when a porcelain crucible was used, even when the precipitate was not previously ignited. When a platinum crucible was used, and the precipitate not previously ignited in the air, the complete reduction to UO_2 occurred within half an hour by igniting it in a current of pure hydrogen over a "blast," and allowing it to cool in an atmosphere of hydrogen over a gradually decreasing flame. The U_3O_8 is a velvety black colored mass, and the UO_2 a dull brown colored mass.

For the above reductions ordinary porcelain and platinum Rose crucibles were used. The hydrogen was purified by Schobig's method,† by first passing it through a strong solution of potassium permanganate to remove the hydrides of arsenic, antimony, phosphorus and carbon; then through a strong solution of caustic soda to remove hydrogen sulphide; and finally through sulphuric acid (sp. gr. 1.84) to remove moisture.

* Roberts-Austen's "Introduction to Metallurgy," p. 54. 1898.

† *Journal für Praktischer Chemie* (2), 14, 289-299.

DETERMINATION OF URANIUM AS PHOSPHATE.

Review of Method.

The precipitation of uranium solution by an alkali phosphate has rarely been employed as a means for the estimation of uranium, probably because the precipitate which forms is gelatinous and difficult to wash free from alkali. This latter trouble has been overcome by adopting the method to volumetric means, which is the reverse of the volumetric estimation of phosphoric acid by the use of a standard uranium solution. The uranium in solution as acetate is titrated by means of a standard solution of sodium-hydrogen-ammonium phosphate ($\text{NaH}\cdot\text{NH}_4\text{PO}_4$) which is added till a drop of the precipitated solution brought in contact with a drop of freshly prepared solution of potassium ferro-cyanide does not give a brown coloration.* The precipitate which forms is $\text{UO}_2\cdot\text{HPO}_4$ in the presence of acetic acid; when ammonia is present some $\text{UO}_2\cdot\text{NH}_4\cdot\text{PO}_4$ also forms. If the solution is acid with hydrochloric acid it must first be neutralized with ammonia and then made acid with acetic acid, as uranyl phosphate is not precipitated from an hydrochloric solution.†

The quantitative estimation of uranium by means of an alkali phosphate was first suggested by Leconte ‡ and later worked out by Pisani.§ The solution of uranium was saturated with ammonia, then acidified with acetic acid and precipitated by an excess of sodium phosphate. The precipitate was allowed to settle from a hot solution, and thoroughly washed by decantation with hot water containing a small amount of ammonium chloride. Pisani stated that the addition of a few drops of chloroform assists the precipitation. The precipitate was dried, and ignited separate from the filter in a platinum crucible. The precipitate after ignition generally had a green tinge which was due to partial reduction of the uranyl phosphate. It should be lemon yellow in color. As a precaution, he always moistened the ignited mass with a few drops of nitric acid, dried, reignited and weighed as $(\text{UO}_2)_2\text{P}_2\text{O}_7$. When

* Mohr's "Lehrbuch der Chemisch-Analytischen Titrimethode, p. 521.

† Dammer's "Handbuch der Anorg. Chemie," 3, 686. 1893.

‡ Leibig and Kopp, "Jahresbericht," p. 642. 1853.

§ *Chemical News*, 3, 211. 1862.

iron or aluminium were present the results were not very good, as more or less of these metals were precipitated along with the uranium. The presence of alkalies and alkaline earth did not interfere with the precipitation.

Crooke * states that when iron is present, the precipitate of uranyl phosphate invariably carries some down with it. In this case the precipitate is a dirty orange-yellow color and granular. By boiling the solution, which is acid with acetic acid, for about twenty minutes the iron is entirely removed, and the solution is colored red by acetate of sesqui-oxide of iron. When the iron is in the "ferrous" state, none is carried down by the uranium.

When the precipitation is made from an acetate solution the precipitate which forms has the formula $UO_2HPO_4 \cdot xH_2O$; when made in the presence of much ammonium salts it is $UO_2NH_4PO_4 \cdot xHO_2$.† Heating facilitates the precipitation of both.

Kitchen ‡ recommends the presence of ammonium acetate, in which uranyl phosphate is almost insoluble. He states that the addition of ammonium chloride causes the precipitate to be more granular and better to wash.

Gibbs § noticed that the gelatinous precipitate of uranyl phosphate formed by di-sodium hydrogen phosphate becomes pulverulent and easily washed by a single evaporation to dryness.

EXPERIMENTAL.

Were it not for the difficulty of washing the greenish-yellow slimy precipitate of uranium phosphate, which is formed by di-sodium hydrogen phosphate, this method would afford a decided advantage over precipitating it with ammonia and weighing it as oxide (U_3O_8), because any error would be greatly diminished by weighing as $(UO_2)_2P_2O_7$. U_3O_8 multiplied by 0.84884 gives the uranium equivalent, while $(UO_2)_2P_2O_7$ multiplied by 0.66815 gives the same; so by weighing the uranium as pyro-phosphate the error or loss is decreased by the ratio of .84884 : .66815.

This method was studied, and the best conditions for weighing

* "Select Methods," 293.

† Fresenius' "Quantitative Chemical Analysis," p. 219. 1900.

‡ Fremy's "Encyclopédie Chimique," p. 85. 1884.

§ *American Journal of Science and Art* (3), 5, 110.

uranium as uranyl pyro-phosphate were worked out, the results of which are tabulated below.

PRECIPITATION OF URANIUM BY DISODIUM HYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution.	Salts added.	Temperature of solution at precipitation.	Crucible in which ignited.	Time of ignition.	Weight of $(\text{UO}_2)_2\text{P}_2\text{O}_7$	Uranium equivalent.	Theoretical amount of uranium taken
1	150 c.c.	$\begin{cases} \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	$\begin{cases} \text{Cold then} \\ \text{heated to B.P.} \end{cases}$	Platinum	15 min.	.2875	.1921	.1925
2	150 "	$\begin{cases} \text{NH}_4\text{Cl} \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	"	10 "	.2884	.1927	.1925
3	150 "	$\begin{cases} \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	Porcelain	10 "	.2878	.1923	.1925
4	150 "	$\begin{cases} \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	$\begin{cases} \text{B.P. for 1 hour} \\ \text{after precipit.} \end{cases}$	Platinum	10 "	.2851	.1905	.1925
5	150 "	$\begin{cases} \text{Chloroform} \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	"	10 "	.2848	.1903	.1925
6	150 "	$\begin{cases} \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	Porcelain	15 "	.2875	.1921	.1925
7	150 "	$\begin{cases} \text{Chloroform} \\ \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \end{cases}$	"	"	20 "	.2870	.1918	.1925

These determinations were made by measuring 50 c.c. of standard uranium nitrate solution into a beaker, diluting to 150 c.c. and adding nitric acid (sp. gr. 1.42)—varying the amount from 0.5 c.c. to 1.5 c.c. The solutions were brought to boiling and ammonia (sp. gr. 0.90) was added to neutral reaction and a measured amount in excess—from 1 c.c. to 10 c.c. The yellow precipitate of ammonium uranate was dissolved by adding 50 per cent. acetic acid till the precipitate disappeared, and then an excess varying from 1 c.c. to 5 c.c. To the solution—which contained besides uranium acetate, an excess of acetic acid, ammonium nitrate and ammonium acetate—was added a saturated solution of di-sodium hydrogen phosphate in excess. The precipitate which formed was greenish white in color and voluminous. The solution was brought to boiling, after which it was allowed to cool and then filtered. In experiments 4 to 7 the solutions were kept for one hour on water-bath, at the temperature of boiling water, after which they were allowed to cool, and then filtered. This treatment assisted the settling of the precipitate, but did not change its gelatinous character.

The washing of the precipitates was done by four decantations and twice on the filter with a hot dilute solution of ammonium

chloride (2.5 grams of salt to 100 c.c. of water). The washing was not so easy as the ammonium uranate precipitates, even when as much as 5 grams of ammonium chloride was added to the solution previous to its precipitation. Neither the addition of chloroform nor of ammonium chloride had any effect on the appearance of the precipitate, as there were already sufficient ammonium salts present, formed by the neutralization of nitric acid by ammonia and of ammonia by acetic acid.

The precipitates, after washing, were dried in at a temperature of from 100° C. to 115° C., separated from the filter paper which was first ignited in the crucible, then the precipitate added and the ignition continued for from ten to twenty minutes at "redness" over a Bunsen burner. The residue in most cases was green in color, due to the partial reduction of uranyl pyro-phosphate. Whenever the temperature of ignition was above "redness" a reduction always occurred, especially so when a platinum crucible was used. When a porcelain crucible was used the ignition could be done at "redness," but above this temperature (as over a "blast") reduction always resulted. The reason that the reduction occurred more readily in a platinum crucible is explained by the fact that platinum is penetrable at high temperatures by hydrogen and hydrocarbons (from the flame). The reduction of U_3O_8 to UO_2 also takes place more readily in platinum, as is shown by previous experiments.

The reduced uranyl pyro-phosphate was not weighed as such, but was moistened with a few drops of nitric acid (sp. gr. 1.42), dried over a low flame and reignited at "low redness" over a Bunsen burner. The mass after such treatment was always a lemon yellow color. The weight of the yellow uranyl pyro-phosphate remained constant, no matter how long it was ignited at a temperature not exceeding "low redness," but above this temperature it always lost weight and assumed a green color. Whenever this occurs it may be reoxidized by again treating it with nitric acid and reigniting at "low redness."

This green residue of pyro-phosphate most probably has the composition $U_2O_3.P_2O_7$, which is indicated by the weights of several which varied from .2820 to .2827 gram. .2820 multiplied by .6833 gives .1929 gram uranium, the theoretical amount of uranium being .1925 gram.

One of the residues which was more intensely ignited than the others, and with the top on the platinum crucible, was of a reddish brown color. Its weight was .2800 gram, showing that the reduction had gone further than $U_2O_3.P_2O_7$, probably approaching $U_2O_2.P_2O_7$.

‡ The composition of the lemon-yellow colored uranyl pyrophosphate is $(UO_2)_2P_2O_7$ or $U_2O_4.P_2O_7$.

Precipitation of Uranium by Ammonium Dihydrogen Phosphate.

As the precipitates formed by disodium hydrogen phosphate were slimy and difficult to wash, it suggested that possibly this difficulty could be overcome by means of an ammonium phosphate. The precipitant used was ammonium dihydrogen phosphate $[NH_4H_2PO_4]$. The mode of procedure was the same as when disodium hydrogen phosphate was used.

To a solution containing .1925 gram of uranium were added from 0.1 c.c. to 1.5 c.c. nitric acid (sp. gr. 1.42) and sufficient water to make 150 c.c. volume. The solution was brought to boiling, ammonia (sp. gr. 0.90) was added to neutral reaction and from 1 c.c. to 10 c.c. in excess. The ammonium uranate which formed was taken into solution by the addition of 50 per cent. acetic acid and from 1 c.c. to 5 c.c. in excess. The solutions, then acid with acetic acid, were brought to boiling and the uranium precipitated by an excess of a saturated solution of ammonium dihydrogen phosphate. The best precipitations, that is, those which were most crystalline and easiest to handle, were formed when about one and a half as much precipitant was added as was necessary for the precipitation. The solutions were boiled for half an hour, and the precipitate allowed to settle before filtering. The precipitates were washed three times by decantation and three times on the filter with a hot dilute solution of ammonium chloride (2 grams salt to 100 c.c. water). The addition of ammonium chloride or of chloroform to the solution was found unnecessary, as enough ammonium salts were already present. The precipitates which formed when ammonium phosphate was used were pulverulent and crystalline, and were as readily filtered and washed as the precipitates of ammonium uranate.

The precipitates were dried, separated from the filter paper and

the paper ignited in a porcelain crucible, after which the precipitate was added and the ignition continued at "redness" for about five minutes. The crucible was allowed to cool and the residue moistened with a few drops of nitric acid (sp. gr. 1.42). The mass was dried over a low flame, then ignited for from 10 to 25 minutes at "low redness" over a Bunsen burner. The mass after this treatment was, in all cases, a lemon-yellow color. The crucibles were allowed to cool in a desiccator, and weighed.

The results obtained are as follows :

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition.	Weight of $(UO_2)_2P_2O_7$.	Uranium equivalent.	Theoretical amount of uranium taken.
8	150 c.c.	$\begin{Bmatrix} NH_4NO_3 \\ NH_4C_2H_3O_2 \end{Bmatrix}$	$\begin{Bmatrix} \text{B. P. boiled} \\ \text{for 1 hour.} \end{Bmatrix}$	Porcelain	10 min.	.2879	.1924	.1925
9	150 "	"	$\begin{Bmatrix} \text{B. P. boiled} \\ \text{for 10 min.} \end{Bmatrix}$	"	15 "	.2880	.1924	.1925
10	200 "	"	$\begin{Bmatrix} \text{B. P. boiled} \\ \text{for } \frac{3}{4} \text{ hour.} \end{Bmatrix}$	"	20 "	.2881	.1925	.1925
11	200 "	"	"	"	20 "	.2879	.1924	.1925
12	150 "	$\begin{Bmatrix} NH_4Cl \\ NH_4NO_3 \\ NH_4C_2H_3O_2 \end{Bmatrix}$	"	"	25 "	.2881	.1925	.1925
13	150 "	$\begin{Bmatrix} NH_4NO_3 \\ NH_4C_2H_3O_2 \end{Bmatrix}$	"	"	25 "	.2883	.1926	.1925
14	200 "	"	"	"	15 "	.2879	.1924	.1925
15	150 "	$\begin{Bmatrix} NH_4Cl \\ NH_4C_2H_3O_2 \end{Bmatrix}$	"	"	15 "	.2878	.1923	.1925
16	150 "	"	"	"	15 "	.2882	.1926	.1925

The filtrates were evaporated and tested for uranium with potassium ferrocyanide. No uranium was indicated.

In several cases when the ignition was done at a temperature above "redness," the precipitate would invariably assume a green color, especially where the residue was in contact with the crucible. Whenever this occurred, the mass was again moistened with a few drops of nitric acid (sp. gr. 1.42), dried over a low flame and reignited at "low redness." By this treatment the mass was oxidized to $(UO_2)_2P_2O_7$.

Several precipitates, after having been weighed as uranyl pyrophosphate, were ignited over a "blast" for about fifteen minutes.

The residue, in all cases, after such treatment were entirely green ; but when moistened with a few drops nitric acid (sp. gr. 1.42) and reignited at "low redness" always changed back to lemon yellow uranyl pyro-phosphate, and their weight was the same as the original weight.

Solution No. 15 was allowed to stand for six days before filtering, in order to determine the solubility of the precipitate. The appearance of the precipitate was the same as those which were filtered directly.

The weighing of uranium as uranyl ammonium phosphate [$UO_2.NH_4.PO_4$] was undertaken, but without success. The filtering through Gooch crucibles was tried, but owing to the fineness of the precipitate this could not be done. After trying to filter six solutions in this manner, the idea of weighing uranium as uranyl ammonium phosphate was abandoned as impracticable.

THE VOLUMETRIC ESTIMATION OF URANIUM.

Belohoubeck,* in 1866, estimated uranium by reducing the solution in a flask with metallic zinc and sulphuric acid. For small amounts of uranium he states that the reduction is complete in about fifteen minutes, while for larger quantities the time required is much longer. The solutions after reduction were diluted, and titrated by a standard potassium permanganate solution, the standard of which was made on ferrous ammonium sulphate.

Sutton † later stated that the estimation of uranium can be conducted with great accuracy by titrating the reduced solution with standard potassium permanganate, in precisely the same way as iron solutions. The uranium should be in solution either as acetate, chloride or sulphate, but not as nitrate. The reduction is best made with zinc and sulphuric acid at a temperature of 50° to 60° C.

Uranium differs from iron, as regards reduction, in that it is not reduced by hydrogen sulphide. When mercuric salts are present the uranium is, however, reduced by this reagent, otherwise it is not. ‡

* *Zeitschrift für Analytische Chemie*, 6, 120. 1867.

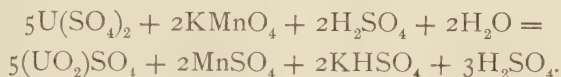
† Sutton's "Volumetric Analysis," p. 375. 1900.

‡ Dammer's "Handbuch der Anorg. Chemie," 3, 686. 1893.

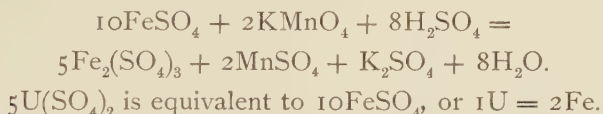
The permanganate solution used for titrating uranium solutions is standardized on iron; two equivalents of iron equal one equivalent of uranium, or $56 \text{ Fe} = 120 \text{ U}$.

When hydrochloric acid solutions of uranium are titrated with potassium permanganate, the amount of free acid present should be less than 3 c.c. to 500 c.c. of uranous solution. Above this amount the results are always high.*

The reaction † which occurs during the titration of sulphate solutions of uranium is :



The reaction which occurs during the titration of ferrous solution is :



The reduction of uranium by zinc and sulphuric acid corresponds to the change of UO_3 to UO_2 .†

C. Zimmerman,§ in 1881, compared the reduction of uranium solutions by zinc and sulphuric acid with the reduction by zinc and hydrochloric acid. He states that uranyl salts in a sulphuric acid solution were reduced by zinc to the uranous state, the reduced liquid assuming a green color. In a hydrochloric acid solution the reduction proceeded still further, to uranium subchloride (U_2Cl_6 or UCl_3), and the solution assumed first a green color and then finally changed to red. The reductions were made in a flask which was closed by a Bunsen valve. After reduction the solutions were diluted to 500 c.c. and titrated with standard potassium permanganate solution, in the presence of from 10 c.c. to 20 c.c. free acid. When hydrochloric acid solutions were titrated, the results were always too high; but when sulphuric acid solutions were titrated, the results were accurate.

* *Zeitschrift für Analyt. Chemie*, 11, 179.

† Mohr's "Lehrbuch der chem.-analyt. Titrimethoden," p. 267.

‡ Watt's "Chemical Dictionary," Vol. 4, p. 820.

§ *Leibig's Annalen der Chemie*, 213, 285-300. 1882.

Zimmerman suggests that the standard permanganate be added in excess and the excess titrated back with a standard ferrous solution. This procedure prevents the oxidation of the uranous salt by air.

EXPERIMENTAL.

The fact that iron is so easily and, at the same time, accurately determined by means of potassium permanganate, and that uranium solutions can be reduced and then oxidized by potassium permanganate, suggested that possibly, with a few modifications, the Belohoubeck method could be adapted to the technical assay of uranium ores.

In order to demonstrate the best means of reducing the uranium solution, several different reducing agents were employed, the results of which are given below :

The first series of experiments was made by reducing the uranyl solution by means of zinc and sulphuric acid at boiling temperature, then by means of zinc and hydrochloric acid.

The second series was made by reducing the uranyl solution by means of a strong solution of stannous chloride and destroying the excess of stannous chloride by adding sufficient mercuric chloride solution, which is the Zimmerman-Reinhart method, so largely used for the estimation of iron.

The third series was made by passing the uranyl solutions through a long Jones' reductor.

The fourth series was made by reducing the uranyl solution by means of strips of metallic aluminium, first in dilute sulphate solutions, then in dilute hydrochloric acid solutions.

The fifth series was made by reducing the uranyl solutions by means of metallic magnesium, first in dilute sulphate, then in dilute hydrochloric acid solutions.

The standard solution of potassium permanganate was made by dissolving 18.96 grams of the salt in distilled water and diluting it to six liters, thus making a $n/100$ solution. The standard was obtained by titrating ferrous sulphate solutions, containing a known quantity of iron.

$$1 \text{ c.c. KMnO}_4 = 0.00548 \text{ gram iron.}$$

The uranium standard was calculated from the iron standard by the equation :

$$239.6 : 2 (55.9) = x : 0.00549 \quad x = 0.01176.$$

Two equivalents of iron correspond to one equivalent of uranium, or the iron standard multiplied by 2.1425 gives the uranium standard. In order to get the uranium standard in terms of U_3O_8 , multiply the iron standard by 2.5243.

The standard of the permanganate solution was verified by taking a measured amount of standard uranium nitrate solution, reducing it with about 50 grams of pure zinc and sulphuric acid [30 c.c. H_2SO_4 (sp. gr. 1.84) in 150 c.c. of solution]. The solution was diluted to 500 c.c. and titrated. The results obtained agreed to the fifth decimal place with those of the iron titration.

Titration of Uranium Solutions with Potassium Permanganate.

Zimmerman* recommends when uranous solutions are titrated with standard potassium permanganate solution that the permanganate be added in excess and the excess then titrated back with a standard solution of ferrous sulphate. He stated that by this procedure the oxidation of the uranous solution by air was prevented. In the following titrations—about sixty in number, and also a number of others made later—the recommendation of Zimmerman was not observed, but the uranous solution was titrated direct in the same manner as a ferrous solution. The oxidation of the uranous solutions was prevented by placing about one gram of dry sodium carbonate in the large Erlenmeyer flask in which the titrations were made. The mouth of the flask was closed by a two and one-half inch funnel, and the solution which was reduced in a small Erlenmeyer flask was emptied into it. The solutions, which were quite acid, on coming in contact with the dry sodium carbonate liberated carbon dioxide which filled the "titration flask" and prevented the oxidation of the uranous solutions by air.

The reductions, whether made by metallic zinc, aluminium or manganese, were made in a small 250 c.c. Erlenmeyer flask, the mouth of which was closed by a small funnel. The uranyl solu-

* *Leibig's Annalen der Chemie*, 213, 300. 1882.

tions were poured into the flask, acidified, the metal added, and the reduction carried on at boiling temperature. After the reduction had occurred, the funnel and sides of flask were washed down with distilled water and the hot solution rapidly emptied into the "titration flask" which contained about one gram of dry sodium carbonate. The flask in which the reduction was made was four times rinsed out with cold distilled water, and the rinsings were poured into the "titration flask," and the solution diluted to from 500 to 600 c.c. The titrations were made at once, adding the permanganate solution till pink "end point," which was very delicate when sulphate solutions were titrated.

The determinations were made as follows: A measured amount of standard uranium nitrate solution was measured into a small beaker, and from 10 to 15 c.c. of sulphuric acid (sp. gr. 1.84), added. The solution was evaporated to dense white fumes, allowed to cool, then poured into an Erlenmeyer flask, which contained a small amount of water. The solution was diluted to a definite volume (100 to 200 c.c.) and more sulphuric acid added.

The best and most rapid reductions occurred when the amount of free sulphuric acid (sp. gr. 1.84) present was within the limits, 1 part acid to 4 parts solution, and 1 part acid to 5 parts solution. When the concentration is more than 1 to 4 the metal, especially zinc is coated with a rather insoluble sulphate which retards the generation of hydrogen.

Comparing the time required for the complete reduction of uranyl solutions with that required for the reduction of iron solutions, it was found to be about twice as long when equivalent amounts of uranium and iron salts were reduced.

When zinc was the metal used for generating the hydrogen, about 50 grams of pure metal (15 lumps) was used.

When the solutions were reduced by means of aluminium, fifteen strips of the metal were used, size 8 mm. wide by 15 mm. long, and 0.5 mm. thick.

The reductions by means of metallic magnesium were made by using eight pieces of a bar (8 mm. in diameter) cut into pieces of 15 mm. length.

The reductions—whether made by means of metallic zinc, aluminium or magnesium—were in all cases the same. The only dif-

ference noticed was the rapidity of solution of the metals; aluminium dissolved more rapid than zinc, and magnesium more rapid than aluminium. The reduction, whether carried on at boiling temperature for one hour, or for as long as five hours, did not go further than $(\text{SO}_4)_2$. The time required for the reduction of about 0.1 gram of uranium by zinc is about one hour, for about 0.2 gram not less than one and a half hours. The uranyl sulphate solution, at first yellow in color, changes to light green and finally to green with bluish tinge—having the appearance of a dilute solution of nickel chloride—which color it retains even though the reduction be continued for as long as four hours.

The results, which were obtained by titrating uranous sulphate solutions, are all that can be desired, as they agree within analytical limits with those obtained by the standard gravimetric method—which is to precipitate the uranium with ammonia, and weigh it as U_3O_8 .

The reduction of hydrochloric acid solutions was also tried. For this purpose, a measured amount of standard uranium nitrate solution was twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry mass of uranyl chloride was taken up with 15 c.c. hydrochloric acid (sp. gr. 1.20), and water added, after which the solution was poured into a small Erlenmeyer flask and diluted to from 100 to 200 c.c. More hydrochloric acid was added, and the solutions reduced at boiling temperature in the same manner as the sulphate solutions. The reductions were made first by the use of metallic zinc, then by metallic aluminium, and lastly by metallic magnesium. In all cases where the reduction was carried on for from two to four hours, it approached (and in several cases reached) the subchloride (U_2Cl_6 or UCl_3). With solutions of about 100 c.c. volume and rather strongly acid (1 part HCl (sp. gr. 1.20) to 4 of solution), at boiling temperature the reduction to UCl_3 was complete within about two hours. By longer treatment the reduction proceeded no further. The color of the hydrochloric acid solution of uranium was at first yellow, changed to green, to bluish green, to olive green, and finally to reddish brown—resembling the color of old port wine. The solutions, previous to titration, were cooled by cold water, diluted to about 600 c.c., and titrated in the same manner as the uranous sulphate solutions.

The "end-point" was not so delicate as when sulphate solutions were titrated. As no "preventative solution" was added, a small amount of chlorine was evolved after the solutions were allowed to remain standing for a few minutes. The interference of the "end-point" by chlorine was prevented by having a very small amount of free hydrochloric acid present, not over 3 per cent. of the total solution.

The results obtained are as follows :

REDUCTION OF URANYL SOLUTIONS BY METALLIC ZINC.

Experiment No.	Dilution at reduction.	Time of reduction.	Dilution at time of titration.	Amount of free acid present.	Amount of KMnO_4 required.	Uranium equivalent.	Theoretical amount of uranium taken.
1	100 c.c.	2 $\frac{3}{4}$ hours	600 c.c.	15 c.c. H_2SO_4	13.10 c.c.	.15406	.1540
2	200 "	3 "	600 "	20 "	13.15 "	.15464	.1540
3	125 "	1 $\frac{1}{4}$ "	500 "	20 "	8.20 "	.09643	.09625
4	135 "	1 $\frac{1}{4}$ "	500 "	25 "	8.20 "	.09643	.09625
5	130 "	1 "	600 "	20 "	16.40 "	.19286	.19250
6	130 "	1 "	600 "	20 "	16.35 "	.19228	.19250
7	125 "	1 $\frac{1}{4}$ "	500 "	20 "	19.60 "	.23050	.2310
8	125 "	1 $\frac{1}{2}$ "	500 "	25 "	19.65 "	.23108	.2310
9	100 "	2 $\frac{1}{2}$ "	600 "	30 c.c. HCl	21.10 "		.1540
10	200 "	2 $\frac{3}{4}$ "	600 "	25 "	19.80 "		.1540

REDUCTION OF URANYL SOLUTIONS BY METALLIC ALUMINIUM.

Experiment No.	Dilution at reduction.	Time of reduction.	Dilution at time of titration.	Amount of free acid present.	Amount of KMnO_4 required.	Uranium equivalent.	Theoretical amount of uranium taken.
11	110 c.c.	$\frac{1}{2}$ hour	600 c.c.	15 c.c. H_2SO_4	13.15 c.c.	.15464	.1540
12	150 "	1 $\frac{1}{2}$ "	600 "	20 "	13.05 "	.15350	.1540
13	150 "	2 $\frac{1}{2}$ "	600 "	20 "	13.10 "	.15406	.1540
14	100 "	2 $\frac{3}{4}$ "	500 "	15 "	13.05 "	.15350	.1540
15	100 "	3 "	500 "	15 "	13.10 "	.15406	.1540
16	200 "	4 "	600 "	25 "	13.15 "	.15464	.1540
17	120 "	1 $\frac{1}{2}$ "	600 "	30 "	13.15 "	.15464	.1540
18	200 "	2 $\frac{1}{2}$ "	600 "	40 "	13.10 "	.15406	.1540
19	200 "	2 $\frac{1}{2}$ "	600 "	50 "	13.15 "	.15464	.1540
20	75 "	1 $\frac{1}{2}$ "	700 "	20 c.c. HCl	20.10 "		.1540
21	75 "	1 $\frac{1}{2}$ "	700 "	20 "	18.85 "		.1540
22	200 "	3 "	700 "	20 "	17.40 "		.1540
23	200 "	3 "	700 "	20 "	19.60 "		.1540

REDUCTION OF URANYL SOLUTIONS BY METALLIC MAGNESIUM.

Experiment No.	Dilution at reduction.	Time of reduction.	Dilution at time of titration.	Amount of free acid present.	Amount KMnO_4 required.	Uranium equivalent.	Theoretical amount of uranium taken.
24	125 c.c.	1 hour	600 c.c.	20 c.c. H_2SO_4	13.10 c.c.	.15407	.1540
25	125 "	1 "	600 "	29 "	13.05 "	.15347	.1540
26	125 "	2 $\frac{1}{4}$ "	700 "	20 c.c. HCl	16.90 "		.1540
27	125 "	2 $\frac{1}{4}$ "	700 "	20 "	17.60 "		.1540

The reduction of uranyl solutions to the uranous state can also be made by passing the solution through a Jones' reductor. The reductor used was much longer than those ordinarily used for the reduction of iron solutions. It was made of a 50 c.c. burette, in the lower part of which was placed an inch layer of broken glass and on top of this was poured an 18-inch column of 20-mesh amalgamated zinc. The amalgamation was done by washing the zinc with a warm dilute solution of mercurous nitrate, then thoroughly washing it with warm distilled water.

The determinations were made by taking a measured amount of standard uranium nitrate solution and evaporating it to dense white fumes with 10 c.c. sulphuric acid (sp. gr. 1.84). The solution was allowed to cool, then diluted to from 100 to 150 c.c. and more sulphuric acid added. The warm solution was poured through the reductor, and caught in a large Erlenmeyer flask which contained about 1 gram of dry sodium carbonate, and the mouth of which was closed by a small funnel. After all the solution had been emptied into the reductor, it was followed by about 250 c.c. distilled water. The solution was then diluted to 500 c.c., and titrated with $n/100$ potassium permanganate solution to faint red end reaction.

The time required for 100 c.c. of uranyl solution and 250 c.c. of water to pass through the reductor was about ten minutes. For 150 c.c. uranyl solution and 250 c.c. of water to pass through it required about twenty minutes.

Sutton* states that while washing the reductor free from iron

* Sutton's "Volumetric Analysis" under Iron.

solutions, the wash water should be kept above the zinc level, so as not to allow of any air-spaces between the successive additions of water, in which case H_2O_2 is formed, thus causing high results. This caution was observed in the reduction of the uranium solutions.

The most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was not less than 1 to 6, nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the sulphate of zinc which formed did not go into solution and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 6, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was within the limits of 1 to 6 and 1 to 5. Even when the solutions were twice run through the reductor no further reduction occurred than when run through once.

The results obtained are shown in the table.

REDUCTION OF URANYL SOLUTIONS BY PASSING THROUGH REDUCTOR.

Experiment No.	Dilution at time of reduction.	Time of reduction.	Dilution at time of titration.	Amount of free acid present.	Amount of $KMnO_4$ required.	Uranium equivalent.	Theoretical amount of uranium taken.
28	100 c.c.	9 minutes.	600 c.c.	20 c.c. H_2SO_4	8.20 c.c.	.09643	.09625
29	100 "	9 "	600 "	15 "	8.20 "	.09643	.09625
30	110 "	10 "	500 "	10 "	13.15 "	.15464	.1540
31	110 "	10 "	500 "	10 "	13.05 "	.15347	.1540
32	115 "	11 "	500 "	15 "	13.10 "	.15407	.1540
33	115 "	11 "	500 "	15 "	13.10 "	.15407	.1540
34	120 "	12 "	500 "	20 "	13.10 "	.15407	.1540
35	120 "	12 "	600 "	20 "	13.10 "	.15407	.1540
36	100 "	10 "	500 "	20 "	16.40 "	.19286	.1925
37	100 "	10 "	600 "	20 "	16.35 "	.19228	.1925
38	125 "	12 "	600 "	25 "	26.20 "	.3081	.3080
39	130 "	14 "	600 "	30 "	26.20 "	.3081	.3080
40	150 "	18 "	600 "	35 "	26.20 "	.3081	.3080
41	110 "	15 "	600 "	15 "	16.40 "	.19286	.1925
42	115 "	18 "	600 "	20 "	16.40 "	.19286	.1925
43	135 "	20 "	600 "	25 "	26.20 "	.3081	.3080

Solutions number 41, 42 and 43 were twice passed through the reductor.

Reduction of Uranyl Solutions by Stannous Chloride.

These reductions were made in the same manner as iron by the Zimmerman-Reinhart method. In some of the reductions, the stannous chloride was allowed to act much longer than is ordinarily done for iron, but the majority of the procedure was the same as the iron reductions. The solutions in the form of nitrate were changed to chloride by twice evaporating to dryness with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry mass of uranyl chloride was taken up with a measured amount of hydrochloric acid (sp. gr. 1.20) and washed into a 750 c.c. Erlenmeyer flask. The solution was heated to boiling and about 0.5 c.c. of an acid solution of stannous chloride was added—three times as much as is required for an equivalent amount of iron. After heating the solution for a given time, the sides of the flask was washed down with water, and 10 c.c. of a saturated solution of mercuric chloride was added. The formation of a silky precipitate of mercurous chloride indicated that sufficient mercuric chloride had been added in order to destroy the excess of stannous chloride. A small amount of dry sodium carbonate was dropped into the flask, the solution diluted to 600 c.c. and 10 c.c. of a "preventative solution" added. The permanganate was added till faint red end reaction.

When a large amount of free hydrochloric acid was present (over 5 per cent.), chlorine gas was evolved after titration and on allowing the solution to stand for a few minutes. When small amounts of free hydrochloric acid were present, the presence of evolved chlorine gas could not be detected by odor.

The color of the uranyl chloride solutions was yellow, but on continued boiling with stannous chloride it changed to green, and on still further boiling to reddish brown. When the solutions were boiled with stannous chloride, a small amount of dry sodium carbonate was added to the flask, the mouth closed by a small funnel, and the boiling continued.

When the reductions were allowed to continue for a minute or so, as for the reduction of ferric solutions, a very slight reduction occurred, but when the reduction was continued for from fifteen minutes to half an hour, the reduction approached and proceeded to the subchloride (UCl_3), the same as when a hydrochloric acid

solution of uranium is reduced by either zinc, aluminium or manganese.

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

Experiment No.	Dilution at time of reduction.	Time of reduction.	Dilution at time of titration.	Amount of free acid present	Amount of KMnO_4 used.	Uranium equivalent.	Theoretical amount of uranium taken.
44 } 45 } 46 }	20 c.c.	$\frac{1}{2}$ minutes.	600 c.c.	15 c.c.	0.6-0.7 c.c.	.00823	.1925
47 } 48 } 49 }	75 "	$\frac{1}{2}$ "	500 "	20 "	0.8-1.5 "	.01764	.1925
50 } 51 }	75 "	$\frac{1}{2}$ "	500 "	20 "	0.4-0.6 "	.00706	.1925
52	35 "	1 "	550 "	35 "	0.8 "	.00941	.1925
53	50 "	1 "	550 "	45 "	2.0 "	.02352	.1925
54	35 "	5 "	600 "	35 "	16.0 "	.18816	.1925
55	50 "	5 "	600 "	45 "	18.5 "	.21756	.1925
56	75 "	10 "	600 "	10 "	4.0 "	.04704	.1925
57	75 "	10 "	600 "	10 "	8.5 "	.09996	.1925
58	35 "	10 "	600 "	25 "	11.0 "	.12936	.1925
59	30 "	10 "	600 "	15 "	15.5 "	.18228	.1925
60	30 "	15 "	600 "	15 "	20.9 "	.24578	.1925

ESTIMATION OF URANIUM IN PITCHBLEND.

In order to apply the preceding separations and determinations,—made on pure solutions,—to an actual commercial assay of pitchblende, samples of the ore were analyzed by two entirely different methods: the Patara method with its several modifications, and the "ether extraction method." In both cases the uranium was determined in several different ways. These assays gave an actual comparison of results, and at the same time tested the separations and estimations of uranium which were worked out on pure solutions.

The assays were first made by Patara's method as follows: Eight samples of the finely divided ore—about 1.3 grams—were weighed into small beakers, and decomposed by adding 5 c.c. water and 10 c.c. nitric acid (sp. gr. 1.42). Complete solution was brought about by heating almost to boiling in covered beakers on a hot asbestos plate till the residues were almost white in color, then the watch glasses were removed and the solutions slowly evaporated to a pasty mass. After cooling, the masses were taken up with 50 c.c. water and 3 c.c. nitric acid (sp. gr. 1.42), and

the solution brought to boiling. The silica was filtered off and washed with boiling water and rejected. The filtrates were diluted to 200 c.c. volume and hydrogen sulphide gas passed through the cold solutions for one hour. The precipitates of sulphides of lead, copper, etc., were filtered, washed with hydrogen sulphide water, and rejected. The filtrates from the sulphides were slowly heated at first and finally boiled in order to expel hydrogen sulphide gas. Evaporation was continued till the bulk of the solutions was about 125 c.c., then the separated sulphur was filtered off and washed. The solutions were brought to boiling and 150 c.c. of a saturated solution of sodium carbonate was added, and boiling continued for twenty minutes, after which the precipitates (principally ferric hydrate) were filtered off and three times washed by decantation and four times on the filter with hot water. The filtrates containing the uranium were evaporated to half volume (about 150 c.c.), slowly neutralized with hydrochloric acid (sp. gr. 1.20) and about 3 c.c. in excess, then boiled for half an hour till all carbon dioxide was expelled. The uranium was precipitated from the hot solutions by means of a slight excess of sodium hydrate (free from carbonate), and boiling for about ten minutes, keeping the beakers covered with watch glasses. The orange-yellow precipitates of sodium uranate were allowed to settle, the supernatant liquids poured through filters, and the precipitates twice washed by decantation and three times on the filters with hot water.

Precipitates No. 1 and No. 2, were dried in a hot oven, separated from the filters and ignited in platinum crucibles, after which the ash of the papers was added to the crucibles and ignition continued at "redness" for five minutes. The residues on cooling were several times treated with hot water, after each treatment pouring the water through a small filter. The filters were dried, ignited, added to the crucibles, and reignited at "redness" for ten minutes. After cooling in a desiccator, they were weighed. According to Patera, the residue consists of $NaO \cdot 2(U_2O_3)$, 100 parts of which contains 88.3 parts of U_3O_8 .

Precipitates No. 3, No. 4, No. 5, No. 6 and No. 7, were dissolved from the filters by warm dilute hydrochloric acid (sp. gr. 1.13), and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10. c.c. hydrochloric

acid (sp. gr. 1.20). The dry residues were taken up with 3 c.c. hydrochloric acid, diluted to 100 c.c. and brought to boiling. The silica, dissolved from the beakers by the strong alkali solution, was filtered off, and washed with boiling water.

Solutions No. 3 and No. 4 were brought to boiling, 5 c.c. hydrochloric acid (sp. gr. 1.20) added and ammonia (sp. gr. 0.90) in excess. The solutions were boiled for fifteen minutes, thus changing the voluminous amorphous precipitate of yellow ammonium uranate into a more crystalline form, darker in color, and which was readily and rapidly washed. The precipitates were allowed to settle, the supernatant liquids poured through filters, and the precipitates three times washed by decantation and twice on the filter with a hot dilute solution of ammonium chloride (2 grams of salt to 100 c.c. water). The precipitates were dried, placed in platinum crucibles and, together with the filter paper, were slowly ignited till the paper was completely destroyed, then ignited in "blast-flame" for ten minutes after which they were slowly cooled in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation to U_3O_8 . They were allowed to thoroughly cool in a desiccator and weighed.

Solution No. 5 was diluted to 150 c.c., brought to boiling and 5 c.c. hydrochloric acid (sp. gr. 1.20) added. The solution was neutralized with ammonia (sp. gr. 0.90) and 5 c.c. in excess. Acetic acid was slowly added to the hot solution, stirring all the while till the yellow precipitate disappeared. The uranium was then precipitated by means of ammonium di-hydrogen phosphate, adding about twice as much as was necessary for complete precipitation. The solution was boiled for fifteen minutes, allowed to cool, then filtered, and the precipitate washed four times on the filter with a hot 2-per-cent. solution of ammonium chloride. The precipitate was dried, separated from the filter paper which was first ignited in a porcelain crucible after which the precipitate was added and ignited at "low-redness" for ten minutes over a Bunsen flame. The crucible was allowed to cool, the residue moistened with a few drops of nitric acid (sp. gr. 1.42), dried on a hot plate, and re-ignited at "low redness" for ten minutes. The lemon yellow

colored precipitate of uranyl pyrophosphate $[(UO_2)_2P_2O_7]$ was weighed, and the U_3O_8 equivalent obtained by multiplying the weight by 0.66815.

Solutions No. 7 and No. 8 were evaporated to about 30 c.c. volume, allowed to cool, 30 c.c. sulphuric acid (sp. gr. 1.84) added, and evaporation continued to dense white fumes. The solutions were poured into 250 c.c. Erlenmeyer flasks, diluted to 150 c.c. and reduced at boiling temperature by about 50 grams of pure granulated zinc. The reductions were continued for one and a half hours till the solutions were a clear green color, resembling that of a dilute solution of nickel chloride. The solutions were then poured into a large Erlenmeyer flask, which contained about one gram of dry sodium carbonate, diluted to 500 c.c. and titrated by $n/100$ potassium permanganate solution.

Precipitate No. 8, of sodium uranate, was dissolved from the filter with warm dilute nitric acid (1 part acid, sp. gr. 1.42 and 2 parts water) and caught in a small beaker. The solution was twice evaporated to dryness, the second time with 10 c.c. nitric acid (sp. gr. 1.42). The dry mass was taken up with 5 c.c. of 50 per cent. acetic acid, diluted to 50 c.c., and the solution boiled till all salts were dissolved. The silica, which was dissolved from the beaker by the strong sodium carbonate solution, was filtered off and washed with hot water. The solution was diluted to exactly 100 c.c. in a graduated flask, 50 c.c. was measured into a large clean platinum dish and the uranium determined by electrolysis as follows: Added 0.5 gram sodium acetate, diluted to 125 c.c. and electrolyzed at a temperature of 65° to 75° C. with a current of $ND_{100} = 0.8$ to 1.0 ampère. The uranium was completely precipitated, as hydrated proto-sesquioxide, within eight hours. The electrolyte was emptied into a beaker, and the black deposit washed with warm water. The electrolyte and the washings were poured through a fluted filter paper, the paper several times rinsed with hot water, dried and ignited on the top of a platinum crucible, and the ash added to the dish. The dish was then dried, ignited over a "blast" for ten minutes, and allowed to cool in a gradually decreasing Bunsen flame. It was placed in a desiccator and, after thoroughly cooling, was weighed. The ignited deposit consisted of U_3O_8 .

The results obtained by this series of assays are as follows :

Experiment No.	Amount of ore taken, grams.	Weighed as:	Weight, gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8 .	Average per cent.
1	1.2863	$NaO(U_3O_8)_2$	.3064	.27055	21.03	20.76
2	1.3278	$NaO(U_3O_8)_2$	.3071	.27117	20.49	
3	1.2882	U_3O_8	.2616	.26160	20.31	20.46
4	1.2880	U_3O_8	.2653	.26530	20.60	
5	1.2840	$(UO_2)_2P_2O_7$	.3297	.25940	20.20	20.20
6	1.4004	Titrated.		.29090	20.77	20.63
7	1.2164	Titrated.		.24940	20.50	
8	.6416	U_3O_8	.1306	.13060	20.36	20.36

Estimation of Uranium in Pitchblende by the Ether Extraction Method.—The ether-extraction method differs from the Patera method in that the uranium is not separated from the fourth group members by means of sodium carbonate, but by ether and ammonium carbonate. The member of this group which has always given the most trouble in effecting a separation is iron, which is associated in large quantities. The iron was separated from uranium and the other metals by shaking the hydrochloric acid solution with ether, free from alcohol. The uranium was then separated from the other associated metals (aluminum, manganese, zinc and nickel) by means of ammonium carbonate.

The procedure was as follows : Seven samples (about 1.3 gram) of the finely divided pitchblende were decomposed with boiling dilute nitric acid (1 part acid, sp. gr. 1.42 and 1 part water) till the residues which remained were almost white in color. The solutions were then evaporated to a pasty mass, taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and twice evaporated to dryness, the second time with 10 c.c. hydrochloric acid (sp. gr. 1.20). The salts were taken up with 5 c.c. hydrochloric acid (sp. gr. 1.20), diluted to 150 c.c. brought to boiling and the silica filtered off and washed. The filtrates were diluted to 250 c.c. and the lead, copper, etc., precipitated as sulphides by passing hydrogen sulphide gas through the cold solutions for about an hour. The filtrates from the sulphides were slowly evaporated to about 150 c.c., and boiled for a few minutes in order to expel all hydrogen sulphide.

The separated sulphur was filtered off and washed. The solutions were brought to boiling, 5 c.c. nitric acid (sp. gr. 1.42) added and boiling continued till the iron was completely oxidized, after which ammonia (sp. gr. 0.90) was added in excess, and boiling continued for fifteen minutes. The precipitates of the metals of the fourth group were filtered off and washed with a warm 2-per-cent. solution of ammonium chloride. The wet precipitates were dissolved from the filters with warm dilute hydrochloric acid (sp. gr. 1.10) and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry salts were taken up with 15 c.c. hydrochloric acid (sp. gr. 1.10), the beakers covered with watch glasses and the solutions heated till all salts had dissolved but not long enough to lose any of the acid by evaporation. After cooling, the solutions were emptied into 250 c.c. separatory funnels, and the beakers rinsed out four times with 5 c.c. hydrochloric acid (sp. gr. 1.10). Fifty c.c. of pure ether, which had been previously shaken up with hydrochloric acid (sp. gr. 1.10), was added to each funnel, and thoroughly shaken for about seven minutes with the aqueous hydrochloric acid solutions, occasionally relieving the pressure which was due to evaporation of ether. After agitation, the funnels were allowed to stand for a few minutes till the two solutions separated, then the lower aqueous layers were run into other separatory funnels. The ether layers, containing most of the iron, were twice shaken up with 5 c.c. hydrochloric acid (sp. gr. 1.10) and the washings added to the main solutions containing the uranium. As all of the iron was not separated by one ether extraction, it was necessary to twice repeat the operation. The second extractions were made with 50 c.c. ether, and the third with 30 c.c. ether. In both cases the ether solutions were twice washed with 5 c.c. hydrochloric acid (sp. gr. 1.10). The aqueous hydrochloric acid solutions, now free from iron, contained a small amount of ether, which was allowed to evaporate spontaneously by exposure. They were then evaporated to about half volume (40 c.c.), diluted to 100 c.c., nearly neutralized with ammonia, and 100 c.c. of a saturated solution of ammonium carbonate added, which precipitated all the metals except uranium. The solutions were slowly boiled for five minutes, filtered, and the precipitates washed with hot water. The

filtrates were evaporated to half volume in order to get rid of most of the carbon dioxide. Yellow precipitates of ammonium uranate separated during boiling, and were dissolved by acidifying the solutions with hydrochloric acid. The solutions were again boiled for about half an hour longer and the uranium determined in four different ways as outlined below.

Solutions No. 9 and No. 10 were precipitated with ammonia in the same manner as solutions No. 3 and No. 4, and the uranium weighed as U_3O_8 .

Solutions No. 11 and No. 12 were precipitated by an excess of ammonium di-hydrogen phosphate the same as solution No. 5. The uranium was weighed as $(UO_2)_2P_2O_7$, and the uranium equivalent obtained by multiplying the weights by 0.66815.

Solutions No. 13 and No. 14 were evaporated to about 20 c.c. volume, 30 c.c. sulphuric acid (sp. gr. 1.84) added, and evaporation continued to dense white fumes. The solutions were then poured into 250 c.c. Erlenmeyer flasks, diluted to 150 c.c. and reduced at boiling temperature by about 50 grams of pure granulated zinc. The reductions were continued for about one and one-half hours till the solutions were a clear green color, similar to that of a dilute solution of nickel chloride. They were then emptied into large Erlenmeyer flasks, which contained one gram of sodium carbonate, diluted to 500 c.c. and titrated by $n/100$ potassium permanganate solution.

Solution No. 15.—The filtrate from the ammonium carbonate precipitation was evaporated to about 50 c.c. volume, acidified with nitric acid (sp. gr. 1.42) and 5 c.c. in excess. Evaporation was continued to dryness, and the dry mass taken up with 5 c.c. of 50 per cent. acetic acid, diluted to 50 c.c. and boiled for ten minutes. The solution was transferred to a 100 c.c. graduated flask, diluted to the mark, 50 c.c. measured into a platinum dish, then diluted to 125 c.c. and 0.5 gram sodium acetate added. The uranium was determined electrolytically by precipitating it with a current of $N.D_{100} = 0.9$ to 1.2 ampère, at a temperature of 65° to $75^\circ C$. At eight hours the uranium was completely precipitated as black hydrated proto-sesquioxide. The deposit was washed with hot water, and the electrolyte and washings poured through a fluted filter in order to catch any particles of the deposit which were de-

tached during washing. The paper was several times rinsed with hot water, dried and ignited on the top of a platinum crucible, and the ash brushed into the dish. The dish was slowly dried over a Bunsen flame and ignited at "redness" for fifteen minutes, after which it was allowed to cool in a desiccator and weighed.

The results obtained by the ether separation method are as follows :

Experiment No.	Amount of ore taken, grams.	Weighed as:	Weight, gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8 .	Average per cent.
9	1.2405	U_3O_8	.2565	.2565	20.67	
10	1.2409	U_3O_8	.2550	.2550	20.55	20.61
11	1.2390	$(UO_2)_2P_2O_7$	.3233	.2545	20.54	
12	1.2991	$(UO_2)_2P_2O_7$	.3431	.2701	20.79	20.66
13	1.2892	Titration.		.2672	20.80	
14	1.2828	Titration.		.2646	20.63	20.71
15	.6207	U_3O_8	.1283	.1283	20.67	20.67

A comparison of these results with those obtained by the Paterson separation shows greater uniformity here. They prove conclusively the advantage of the ether separation where accuracy is required, and also show that this latter method is the method to employ when the introduction of alkali salts is undesirable. The time required is the same. The ether separation is more accurate, but more expensive. The greater part of the ether can, however, be saved by distilling from the iron solutions and again using it for other separations.

SUMMARY OF RESULTS.

The conclusions drawn from this investigation on the separation and determination of uranium, briefly stated, are as follows :

1. In order to separate uranium (and the other members of group four) from the metals of groups five and six, the solution should contain not over one part of concentrated acid (either hydrochloric or nitric acid) in fifty parts of solution ; that is, not over 2 per cent. of concentrated nitric acid or hydrochloric acid should be present.

2. The separation of uranium from the metals of groups three and four is best accomplished by means of either a saturated solu-

tion of sodium carbonate, or else by ether followed by a saturated solution of ammonium carbonate. The latter method is preferable when the introduction of fixed alkalis is undesirable.

3. The ether extraction method for the separation of uranium from iron depends on the fact that ferric chloride is extracted from an aqueous hydrochloric acid solution, whereas the uranyl chloride is retained in the aqueous solution. For this separation it is necessary that the hydrochloric acid used for the solution be of specific gravity 1.10 and that three ether extractions be made. The ether used should be free from alcohol, and also previously shaken up with hydrochloric acid (sp. gr. 1.10).

4. The separation of uranium from iron by means of ammonium carbonate or alkali bicarbonates is not complete as some iron goes into solution with the uranium, and can only be completely separated by adding ammonium sulphide, by largely diluting the solution, or else by allowing the solution to stand exposed for a long time. These methods give much trouble, especially so the last, in which case the iron separates as a basic ferric hydrate, which is difficult to handle. Use the normal fixed alkali carbonates instead of ammonium carbonate, or alkali bicarbonates.

5. The separation of uranium from iron by means of sodium carbonate is complete, provided a large excess of a saturated solution of sodium carbonate be used, and the solution boiled for at least fifteen minutes after the precipitation. The boiling is necessary in order to get all the uranium into solution. By such treatment, no uranium remains with the iron, which is completely precipitated as ferric hydrate in a form readily filtered and washed.

6. The separation of uranium from the alkalies and alkaline earths by means of electrolysis is complete, easily accomplished and gives accurate results. The best conditions for this separation are as follows: The solution, containing not over .15 gram of U_3O_8 is acidified with 50 per cent. acetic acid and 2 c.c. in excess. Dilute to 125 c.c. and electrolyze at a temperature of 60 to 75° C. with a current of $N.D_{100} = 0.7$ to 1.0 ampère. The precipitation is complete within about eight hours.

7. The separation of uranium from the alkalies and alkaline earths is accomplished by precipitating the uranium three times from hot solution with ammonia in the presence of ammonium chloride.

8. The separation of uranium from the alkalis and alkaline earths by means of an excess of ammonium phosphate in the presence of ammonium acetate is complete. The precipitations should be made from a hot solution and the boiling continued for at least fifteen minutes.

9. The yellow slimy voluminous amorphous precipitate of ammonium uranate,—formed by precipitating uranium with ammonia in the presence of an ammonium salt,—is converted into a darker yellow colored crystalline form by boiling it for about twenty minutes, and then allowing it to settle in the cold.

10. The separation of the filter paper from the precipitate of ammonium uranate for the purpose of igniting to UO_2 or U_3O_8 is unnecessary. The precipitates together with the filter are at first slowly ignited till the paper is destroyed, then the ignition is continued in the ordinary manner.

11. The complete oxidation of uranium to U_3O_8 is accomplished by igniting ammonium uranate, in either a platinum or porcelain crucible, over a "blast." This is done by having the crucible in a slanting position and igniting intensely over a "blast" for about ten minutes, after which the crucible is allowed to cool in a slowly decreasing Bunsen flame.

12. The reduction of U_3O_8 to UO_2 , as recommended by Rose for the purpose of control, could not be done by igniting it intensely in an atmosphere of pure hydrogen. The reduction was less complete when the ignition was done in a porcelain crucible than when done in platinum. This seems to be explained by the fact that platinum at high temperatures is penetrable by hydrocarbons. The hydrocarbons of the flame, in this case, assisting the reduction.

13. The estimation of uranium as phosphate is easily and accurately done when the precipitant used is ammonium phosphate, in the presence of ammonium acetate. The precipitate of $UO_2 \cdot NH_4PO_4$ on boiling becomes crystalline, and is easily filtered and washed. The ignited precipitate previous to weighing should be moistened with a few drops of nitric acid (sp. gr. 1.42), dried and re-ignited at "low redness" in a porcelain crucible. Above this temperature, and especially so in platinum, a reduction of the $(UO_2)_2P_2O_7$ always occurs. Whenever reduction occurs it may be

re-oxidized to $(UO_2)_2P_2O_7$ by moistening the greenish mass with a few drops of nitric acid (sp. gr. 1.42) and re-igniting at "low redness." The ignitions should be done in porcelain.

14. The most rapid determination of uranium is accomplished by reducing a sulphate solution by means of pure metallic zinc and titrating it with standard potassium permanganate solution in an atmosphere of carbon dioxide. The reductions, whether made by means of metallic zinc, aluminium, magnesium, or in a long Jones' reductor, were in all cases complete, and the results obtained were concordant with those obtained gravimetrically.

15. When hydrochloric acid solutions of uranium are reduced by means of metallic zinc, aluminium, magnesium, or stannous chloride, the reduction goes lower than UCl_4 . It approached and in several cases reached the subchloride UCl_3 . So the titration of hydrochloric acid solutions of uranium by standard potassium permanganate should not be employed as a means of estimating uranium.

BIOGRAPHICAL.

Edward Frank Kern entered the University of Tennessee at Knoxville in September, 1893, and graduated in June, 1897, receiving the degree of B. S. in chemistry. Remained one year longer continuing work in the sciences and literature. Entered the University of Pennsylvania at Philadelphia in October, 1898, and remained there till June, 1900, doing graduate work in chemistry. October, 1900, to June, 1901, studied for the degree of Ph.D. at Columbia University in the City of New York.

Publications: "The Titration of Iron Salts in the Presence of Hydrochloric Acid" in "University of Tennessee Magazine," October, 1898.

"The Electric Current in Chemical Analysis" in "University of Tennessee Record," April, 1901.

"A Comparison of the Methods for the Electrolytic Precipitation of Iron."

"A New Method for the Electrolytic Precipitation of Nickel and Cobalt from Cyanide Solutions."

The last two articles were read April 12, 1901, before the New York Section of the American Chemical Society.

